Ni/TiO$_2$ Ultraviolet Detector

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Abstract. The fabrication technology of solid-state photon detectors based on semiconductors other than silicon is yet to mature, but their recent progress opens new possibilities. Such devices are especially attractive for ultraviolet radiation level measurements because semiconductor materials with band gaps larger than 3.0 eV can be used as “visible-blind” detectors, the operation of which do not require using visible light filters. Here, fabrication and characterization of a UV detector based on nickel/titanium dioxide Schottky junction is reported. The operation of the device is described based on the photoelectric mechanism taking place in the carrier-depleted oxide adjacent to the Ni layer. Simplicity of fabrication, cost-effectiveness and fast response are the positive features of the device. These features of the device are compared with those of the previously reported Ag/TiO$_2$ UV detectors.

1. Introduction

Recent civil and military applications of ultraviolet (UV) detectors [1], such as solar UV level monitoring [2], biological and chemical process measurement [3], flame sensors [4] and secure non-line-of-sight communication [5] have made researchers to develop varieties of UV detectors. Wide band-gap semiconductors such as ZnO, SiC, GaN and TiO$_2$ are becoming dominant in UV photodetector fabrication since they are intrinsically visible-blind, working properly in hostile environments and enabling room temperature operation. Among these semiconductors, TiO$_2$ has been considered for many optoelectronic applications including photocatalysis and solar energy conversion [6, 7] owing to its facile preparation and low cost fabrication process. TiO$_2$ band gap is 3.2 eV for its anatase phase and 3.0 eV for the rutile. Such a wide band gap makes TiO$_2$ suitable for UV detection as it is insensitive to the background visible and infrared lights.

Different structures are used for photodetector fabrication, among which Schottky-type metal-semiconductor junctions, due to their simple manufacture, absence of high temperature diffusion process and its high speed of response are common [8]. The most prominent parameter of a Schottky photodiode is its Schottky barrier height. For a metal connected to an n-type semiconductor of smaller work function, the Schottky barrier ($\Phi_b$) is defined by [9-11]:

$$\phi_b = \phi_m - \chi_s$$  \hspace{1cm} (1)

Where, $\Phi_m$ is the metal work function and $\chi_s$ is the semiconductor electron affinity. As TiO$_2$ work function ($\phi_{TiO2}=4.6$ eV for rutile phase [12]) is smaller than nickel work function ($\phi_{Ni}=5.1$ eV [13]), Ni/TiO$_2$ contact acts as a Schottky diode. Assuming that the electron affinity of TiO$_2$ is 3.9 eV [14], according to (1), the barrier height formed at the Ni/TiO$_2$ interface is 1.2 eV.
Taking the nickel contact layer thin enough (50 nm), it allows UV photons to reach the carrier depletion region at the Ni/TiO$_2$ contact and generate carriers to participate in the device current. Photons with energies more than 3 eV, if absorbed in the depletion region of the oxide layer, would generate electron-hole-pairs (EHP) because of the band-to-band excitation in the semiconductor. The generated carriers are swept in different directions by the internal electric field and participate in the device current. The light photons with photon energy less than 3 eV cannot be absorbed in the device and create zero current.

In this work, the current-voltage characteristics and the UV photoelectric properties, such as photo response, response time and spectral response of Ni/TiO$_2$ junctions fabricated on thermally oxidized titanium chips are reported. The results demonstrate that the Ni/TiO$_2$ UV sensor responds much faster than other similar devices.

2. Experimental

Pure titanium foil (99.7% purity, 0.9 mm thick) is cut into 8 mm×8 mm chips. The chips are polished and then cleaned by the means of ultrasonification in acetone for five minutes followed by rinsing with deionized water and drying with nitrogen. The rutile layer is grown thermally on titanium substrate in an electric furnace at 700°C in clean air for 30 minutes. SEM micrograph of the oxidized surface is shown in Figure 1. The electrical contact between the native oxide layer and the titanium substrate is supposed to be an ohmic contact since the work function of titanium and titanium dioxide are reported to be 4.3 [13] and 4.6 eV [12], respectively. The Ni/TiO$_2$ contact is formed by thermal evaporation of 45 nm thick nickel thin film on to the surface of titanium dioxide layer. The contact area is 2 mm$^2$. Two wire segments are attached by silver paste to the Ti and Ni electrodes. The Ni-TiO$_2$-Ti structure of the device is schematically given in Figure 2.

![SEM image of the TiO$_2$ layer grown by the oxidation of the titanium chip at 700°C for 30 min in air.](image)

**Figure 1.** SEM image of the TiO$_2$ layer grown by the oxidation of the titanium chip at 700°C for 30 min in air.
Source measure unit (SMU), Keithly 238, and lambda EZ 201 monochromator are utilized for measuring the current vs. voltage (I-V) characteristic and spectral response of the device, respectively. To measure the relationship between the photo current and UV light intensity, the device is exposed to a UV LED. The transient photo response is measured by a sampling oscilloscope, Arma D-1040. All measurement is carried out at room temperature.

3. Results and discussion

3.1. Electrical Properties of Ni-TiO$_2$ contact

Current-voltage characteristics measured by SMU for Ni/TiO$_2$ Schottky contact before and after 15 minutes annealing at 190°C under -300 mV biasing voltage are shown in Figure 3 and Figure 4, respectively. For better visualization, Figure 5 shows the I-V characteristics in a semi-logarithmic scale. As it is clear in the Figures 3-5, rectification increases 4 times after annealing. The role of thermal annealing in air in junction barrier formation is described by Hossein-Babaei et al. based on the physicochemical parameters of the constituting materials [9]. The contact behavior can be explained based on the thermionic emission theory. The barrier height is defined by

$$\phi = \frac{kT}{q} \ln(A^*T^2/I_s)$$

(2)

Where $k$ is the Boltzmann constant, $T$ is the operating temperature, $A$ is the junction area, $A^*$ is the TiO$_2$ Richardson constant and $I_s$ is the reverse saturation current. With $A^*=1200$ A.cm$^2$/K$^2$ for TiO$_2$ [15] and assuming $V > 3kT/q$, the effective barrier height is found to be 1.1 eV. The energy band diagrams of Ni-TiO$_2$ junction is shown in Figure 6. Based on this diagram the barrier height equals 1.2 eV that is about 10% wider than the theoretically predicted energy gap.

![Figure 2. The schematic diagram of the Ni/TiO$_2$ sample.](image)

![Figure 3. I-V characteristics of an as-fabricated Ni-TiO$_2$ diode at room temperature.](image)
**Figure 4.** I-V characteristics of the Ni/TiO$_2$ diode after thermal annealing at 190°C in air.

**Figure 5.** Semi logarithmic Current-voltage characteristics of the Ni-TiO$_2$ diode annealed at 190°C

**Figure 6.** The proposed energy band diagram of the Ni/TiO$_2$ contact.
3.2. Photoelectric properties of Ni-TiO$_2$ contact

To study the photosensitivity of the diode, I-V characteristics are measured under varying light intensities. The results are presented in Figure 7. As expected, the reverse current of the diode, which is the sum of the thermal current and photo current, crosses the I-axis at negative values proportional to the light intensity. The relationship between voltage and current can be attributed to the presence of traps which release carriers at higher voltages [16]. Figure 8 is the spectral response measured at -300 mV biasing voltage for the TiO$_2$ photo detector with nickel Schottky contact. The photoresponse has a high magnitude over the band gap and a cut-off at wavelength around the absorption edge of the rutile phase TiO$_2$ (~405 nm) [17]. Because of high absorption coefficient at higher wavelengths, the photoresponse drops as the absorption result in generation of EHPs far away from the depletion region. These EHPs have a higher probability of recombination before participating in the photocurrent [18]. Therefore, this device shows the highest sensitivity at 365 nm.

To study the stability of the optoelectronic features, the sample devices are exposed to UV light at wavelength of 365 nm continuously for 16 hours. It was found that the photoresponse of the device reaches to 98% of its primary state after 16 hours. The temporal response of the device is displayed in Figure 9. The device shows a fast time response with a response time of 10 ms and a recovery time of 120 ms. However, in Ni-TiO$_2$–Ni UV resistive detectors the rise and recovery times are reported to be 13 ms and 11000 ms, respectively [19].

![Figure 7. The reverse current of the Ni/TiO$_2$ diode under different UV light (at 390 nm) intensities and biasing voltages.](image)

![Figure 8. The spectral response of the Ni/TiO$_2$ photodiode.](image)
4. Summary
The fabrication of a Ni-TiO$_2$ UV detector was reported. Our electrical measurements indicate that the as-fabricated Ni-TiO$_2$ contact has zero junction energy barrier. However, a thermal annealing process in air causes drastic changes in the device behavior. After annealing, a Shottky barrier height of 1.0 eV was observed, which is close to the 1.2 eV calculated by the difference of the metal work function and electron affinity of the oxide. The fabricated UV detector shows stable photoresponse. The maximum photoresponse is 2 mA/W at 365 nm. Fast rise and recovery times of 10ms and 120 ms were measured respectively.

References
[1] Hossein-Babaei F, Lajvardi M M and Boroumand F A 2012 Sens Actuators A 173 116
[2] Lajvardi M M and Boroumand F A 2013 Environmental UV-A Level Monitoring Using an Ag-TiO$_2$ Schottky Diode Key Engineering Materials 543 113-6
[3] Zeskind B J et al. 2007 Nucleic acid and protein mass mapping by live-cell deep-ultraviolet microscopy Nature Methods 4 567-9
[4] Perera A G U et al. 2007 Performance improvements of ultraviolet/infrared dual-band detectors Infrared physics & technology 50 142-8
[5] Ding H, Chen G, Majumdar A K, Sadler B M and Xu Z 2009 Modeling of non-line-of-sight ultraviolet scattering channels for communication Selected Areas in Communications, IEEE Journal on 27 1535-44
[6] Nosaka A Y, Kojima E, Fujiwara T, Yagi H, Akutsu H and Nosaka Y 2003 Photoinduced changes of adsorbed water on a TiO$_2$ photocatalytic film as studied by 1H NMR spectroscopy J. of Phys. Chem. B 107 12042-4
[7] Grätzel M 2001 Photoelectrochemical cells Nature 414 338-44
[8] Goushcha A and Tabbert B 2007 Optical Detectors Springer Handbook of Lasers and Optics 503-62
[9] Hossein-Babaei F, Lajvardi M M and Alaei-Sheini N 2015 The energy barrier at noble metal/TiO$_2$ junctions Appl. Phys. Lett. 106 083503
[10] Hossein-Babaei F and Rahbarpour S 2011 Titanium and silver contacts on thermally oxidized titanium chip: electrical and gas sensing properties Solid-State Electronics 56 185-90
[11] Hossein-Babaei F and Rahbarpour S 2011 Separate assessment of chemoresistivity and Schottky-type gas sensitivity in M–metal oxide–M' structures Sens and Actuators B: Chemical 160 174-80

Figure 9. Transient response of the Ni/TiO$_2$ UV sensor.
[12] Schierbaum K D, Kirner U K, Geiger J F and Göpel W 1991 Schottky-barrier and conductivity
gas sensors based upon Pd/SnO$_2$ and Pt/TiO$_2$ Sensors and Actuators B: Chemical 4 87-94
[13] Jakobi K, 3.1.2.4 Work Function Data, Ed. by G. Chiarotti, Springer Materials. The Landolt-
Börnstein Database http://www.springermaterials.com DOI:10.1007/10086058_16
[14] Könenkamp R and Rieck I 2000 Electrical properties of schottky diodes on nano-porous TiO$_2$
films Materials Science and Engineering: B 69 519-21
[15] Tang J, White M, Stucky G D and McFarland E W 2003 Electrochemical fabrication of large-
area Au/TiO$_2$ junctions Electrochemistry communications 5 497-501
[16] Frenkel J 1938 On pre-breakdown phenomena in insulators and electronic semi-conductors. Physical Review 54 647
[17] Stamate M, Vascan I, Lazar I, Lazar G, Caraman I and Caraman M 2005 Optical and surface
properties TiO$_2$ thin films deposited by DC magnetron sputtering method J. Optoelectronics and Advanced Materials 7 771-4
[18] Tomás S A, Luna-Resendis A, Cortés-Cuautli L C and Jacinto D 2009 Optical and morphological
characterization of photocatalytic TiO$_2$ thin films doped with silver Thin Solid Films 518 1337-40
[19] Kong X et al. 2009 Metal-semiconductor-metal TiO$_2$ ultraviolet detectors with Ni electrodes Appl. Phys. Lett. 94 123502