



## Letter

Effects of surface self-assembled  $\text{NH}_4^+$  on the performance of  $\text{TiO}_2$ -based ultraviolet photodetectorsGuohua Liu<sup>a</sup>, Chen Tao<sup>a</sup>, Min Zhang<sup>b</sup>, Xuehui Gu<sup>a</sup>, Fanxu Meng<sup>b</sup>, Xindong Zhang<sup>a,\*</sup>, Yu Chen<sup>c,\*</sup>, Shengping Ruan<sup>a,\*</sup><sup>a</sup>State Key Laboratory on Integrated Optoelectronics, Jilin University, Changchun 130012, China<sup>b</sup>College of Electronic Science and Engineering, Jilin University, Changchun 130012, China<sup>c</sup>Institute of Semiconductors, Chinese Academy of Sciences, Beijing 100083, China

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## ABSTRACT

In this letter, a metal–semiconductor–metal ultraviolet photodetector based on  $\text{NH}_4^+$  modified  $\text{TiO}_2$  film was fabricated. The barrier height between  $\text{TiO}_2$  and Au electrode was lowered due to the self-assembled  $\text{NH}_4^+$  on  $\text{TiO}_2$  surface, leading to a significant improvement in the device performance. At 5 V bias, a photocurrent of 84.93  $\mu\text{A}$  and a responsivity of 361.07 A/W were obtained under the irradiation of 300 nm UV light. The dark current was merely 88.8 pA, two orders of magnitude lower than that of the  $\text{TiO}_2$  device (2.85 nA). The rise time was sharply shortened from 2.735 s to 366.9 ms. The ratio of photocurrent to dark current was nearly 6 orders of magnitude.

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## 1. Introduction

Ultraviolet photodetectors (UVPDs) have drawn much attention due to their broad applications in light-wave communication, flame detection, imaging techniques, as well as in optoelectronic integrated circuits [1–5]. Various wide band-gap semiconductors have been investigated for UVPDs because of their intrinsic visible-blindness, chemical and thermal stability, which are advantages for devices operating in harsh environments [6–8]. Extensive researches have been devoted to improving the performance of UVPDs based on wide band-gap semiconductors, such as doping [9,10], new synthesis method of matrix materials [11,7] and improvement of device structures [12,13]. However, these methods always introduce complicated preparing processes and fabrication techniques. In addition, the UVPDs still exhibited relatively large dark current and long response time.

Surface modification, by contrast, is a comparatively simple and efficient way to enhance the performance of photoelectric devices via manipulating charge transport [14–16]. Solution-processed interfacial materials, including some sulphides [17], polymers [18] and nonconjugated polyelectrolytes [19], have been demonstrated as good modifying materials in the applications for UVPDs

and light-emitting devices. The electrical and optical characteristics of the devices were found to be dramatically improved. However, up to now few reports have focused on the modification of self-assembled  $\text{NH}_4^+$  on  $\text{TiO}_2$  surface to enhance UVPDs' performance.

$\text{TiO}_2$ , as a wide band-gap (3.0–3.2 eV) oxide semiconductor, has showed superiority in UV detection because of its low cost and outstanding electro-optical characteristics [20–22]. In this paper, a metal–semiconductor–metal  $\text{TiO}_2$  UVPD with Au electrodes was fabricated on quartz substrates. By removing part of the dangling bonds of oxygen atoms on  $\text{TiO}_2$  surface and subsequently forming interfacial binding states that are similar to a kind of “dipoles”, the performance of the device has been significantly enhanced. X-ray photoelectron spectroscopy (XPS) provided a clear evidence for the dipole formation between  $\text{NH}_4^+$  and exposed oxygen ions on  $\text{TiO}_2$  surface, which led to the decrease in the Schottky barrier height (SBH) between  $\text{TiO}_2$  and Au.

## 2. Experimental details

The experimental procedure involved (1) the preparation and modification of  $\text{TiO}_2$  films and (2) the fabrication of UVPDs.  $\text{TiO}_2$ -sol was prepared by a simple sol–gel method through the precursor reaction in a conical flask. In a typical procedure, 8 ml tetrabutyl titanate [ $\text{Ti}(\text{OC}_4\text{H}_9)_4$ ] was dissolved in 100 ml ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ), followed by the sequential addition of 6 ml acetic acid ( $\text{CH}_3\text{COOH}$ ), 8 ml acetylacetone, and 8 ml deionized (DI) water. The mixture was kept stirring at room temperature for 2 h. After aging for a period of time, the  $\text{TiO}_2$ -sol was spun cast on cleaned quartz substrates at 2800 r/min for 20 s. The spin-coating process was repeated for another 4 times. The samples were then annealed at 600 °C for

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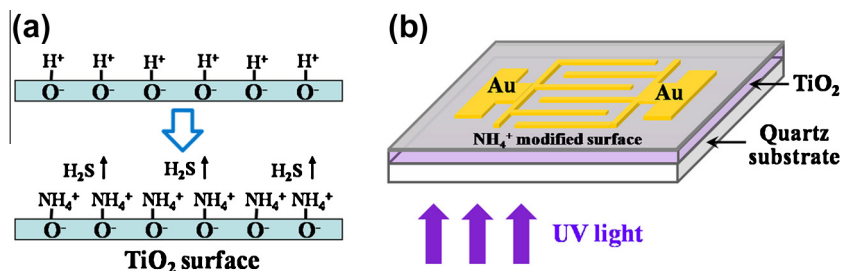


Fig. 1. (a) The self-assembled process on  $\text{TiO}_2$  surface. (b) The structure of a modified  $\text{TiO}_2$ -based UVPD.

2 h in a muffle furnace to form polycrystalline oxide films. After that, we immersed the  $\text{TiO}_2$  thin films into the diluted hydrochloric acid (10%) for 10 h. After being washed with DI water for several times, the samples were subsequently immersed in ammonium sulfide  $[(\text{NH}_4)_2\text{S}]$  solution (16%) for 30 min. The modified  $\text{TiO}_2$  films were then washed with DI water and dried in nitrogen flow.

Based on the thin films mentioned above, interdigitated MSM (Au/ $\text{TiO}_2$ /Au) circular structures were fabricated. Au films were deposited by radio frequency magnetron sputtering and electrodes were prepared with photolithography and lift-off technique. X-ray photoelectron spectroscopy (XPS) was performed using a British photoelectron spectrometer (VG ESCA LAB MKII). The UV–Vis absorption spectra were obtained using a Shimadzu UV-1700 Pharma Spec UV spectrophotometer. A 30-W deuterium lamp and a monochromator were combined to provide the monochromatic light. The current–voltage ( $I$ – $V$ ) characteristics and photoresponse spectra were measured using a Keithley 2601 source meter together with a UV power meter. The response time was recorded using an oscilloscope.

### 3. Results and discussion

Fig. 1(a) shows the self-assembled process occurred on  $\text{TiO}_2$  surface. Because of the existence of crystal boundary, periodic potential field of lattice atoms is interrupted so that negatively charged dangling bonds of oxygen atoms are exposed on the surface of the  $\text{TiO}_2$  thin film. Due to electrostatic attraction, these exposed oxygen ions can adsorb hydrogen ions ( $\text{H}^+$ ) from the dilute acid solution, which makes  $\text{TiO}_2$  surface exhibit cationic characteristics. Once  $(\text{NH}_4)_2\text{S}$  aqueous solution covers the “acidic”  $\text{TiO}_2$  surface, the self-assembled process occurs. Ammonium ions

$(\text{NH}_4^+)$  would take the places of  $\text{H}^+$  to form binding states with oxygen ion, which are similar to a kind of “dipoles”. The direction of the surface electric dipole moment is opposite to that of the built-in electric field in the space charge region, consequently leading to a reduction of the SBH between  $\text{TiO}_2$  and Au. The photocurrent of the device can be improved and hence, a higher photoresponsivity is obtained [23]. Fig. 1(b) illustrates the device structure. It is worth mentioning that the effects of possible exposed titanium ions on  $\text{TiO}_2$  surface are not considered, since due to their metallic characteristic they may easily bond with oxygen in the air during the high-temperature annealing process.

To support our analysis, XPS measurements were performed for the two samples:  $\text{TiO}_2$  and  $\text{NH}_4^+$  modified  $\text{TiO}_2$ . Fig. 2 shows the high-resolution XPS spectra for Ti 2p, N 1s and O 1s. The Ti 2p core level spectra of the films are presented in Fig. 2(a). The peak position and intensity of Ti 2p change little before and after modification, indicating that the chemical status of Ti is scarcely influenced by the modified process. There are two asymmetric N 1s peaks centered at 398.6 eV and 400.1 eV, as illustrated in Fig. 2(b), which can be assigned to the nitrogen atoms in the neutral amines residual on the surface and the self-assembled  $\text{NH}_4^+$ , respectively [18,19,24,25]. The O 1s spectra show that the intensity of the peak at 529.6 eV, which reflects the number of free dangling bond of oxygen atoms on  $\text{TiO}_2$  surface, decreases after  $\text{NH}_4^+$  modification. Moreover, a shoulder is observed at higher binding energy (about 531 eV) after

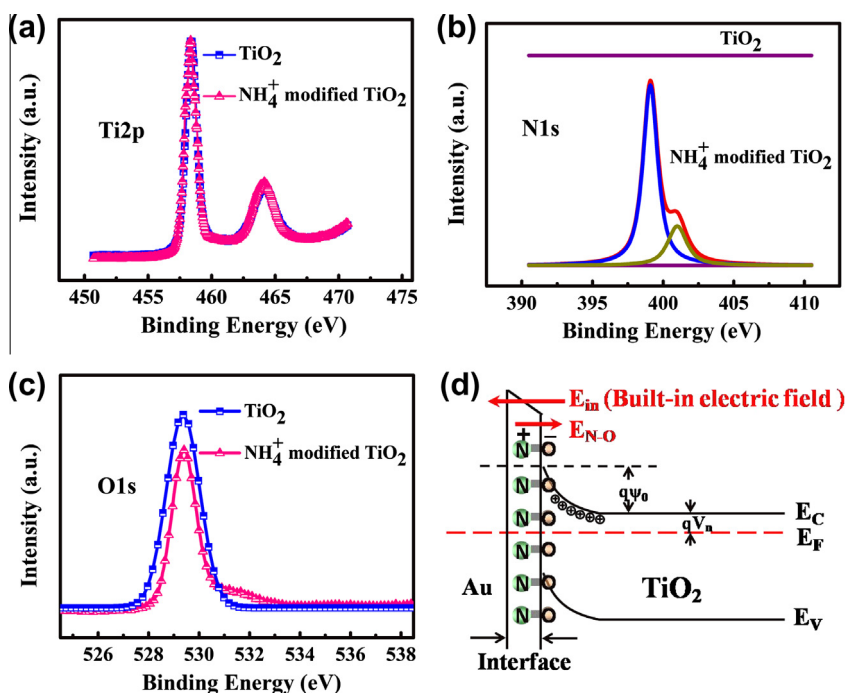


Fig. 2. The high-resolution XPS spectra for  $\text{TiO}_2$  and modified  $\text{TiO}_2$  films: (a) Ti 2p, (b) N 1s, (c) O 1s. (d) Schematic energy band diagram of Au/ $\text{TiO}_2$  contact after modification.

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