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# Influences of surface capping with electrostatically self-assembled PEI on photoresponse of TiO<sub>2</sub> thin film†

Xuehui Gu,<sup>‡a</sup> Fanxu Meng,<sup>‡a</sup> Guohua Liu,<sup>b</sup> Haifeng Zhang,<sup>c</sup> Jingran Zhou,<sup>\*a</sup> and Shengping Ruan<sup>\*b</sup>

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The photoresponse of TiO<sub>2</sub> thin film was significantly improved due to the decrease of Schottky barrier height between Au and TiO<sub>2</sub> via the formation of interface dipoles, which was caused by electrostatically self-assembled PEI on the surface of TiO<sub>2</sub> film.

Ultraviolet photodetectors (UVPDs) have attracted much interest due to their wide applications in light-wave communications, imaging techniques, flame sensing, as well as in future memory storage and optoelectronic circuits.<sup>1-3</sup> Various wide band-gap semiconductors (such as II-VI compounds, III-nitrides, IV-VI compounds, *etc.*) have been investigated for UVPDs due to their intrinsic visible-blindness, chemical and thermal stability, which is an advantage for devices operating in harsh environments.<sup>4-9</sup> In recent years, extensive research has been devoted in improving the responsivity and the photocurrent of UVPDs based on wide band-gap semiconductors: 1) synthesis of low dimensional materials,<sup>1,10</sup> 2) preparation of doped materials,<sup>11,12</sup> However, these methods will introduce complicated fabrication processes. Interface modification, by contrast, has become more and more popular, which provides a comparatively simple and efficient way to enhance the performance of UVPDs via manipulating the charge transport.<sup>13,14</sup>

Solution-processed organic interfacial materials, which can alter the work function (WF) on the surface of semiconductor materials by forming extremely thin interfacial dipoles (typically 1-2 nm), have been demonstrated good substitute for inorganic counterparts in inverted polymer solar cells and light-emitting devices,<sup>15-19</sup> especially the nonconjugated polyelectrolytes (NPEs) due to their high stability, easier synthesis procedure than conjugated polyelectrolytes, and unique film formation characteristics of ionic self-assembly onto oppositely charged surfaces.<sup>20,21</sup> However, the application of NPEs in UVPDs has been seldom reported. As the Schottky barrier between metal electrodes and wide band-gap semiconductors can be tuned with the variation of WF on the surface of semiconductors, NPEs can be expected to be ideal interfacial materials for photodetectors.

In this communication, metal-semiconductor-metal (MSM) TiO<sub>2</sub> thin-film UV detectors with Au electrodes were fabricated on quartz substrates. By introducing polyethyleneimine (PEI, a very simple type of cationic NPEs) as an interfacial layer between Au electrode and n-type TiO<sub>2</sub> film, the photocurrent and response speed was significantly enhanced. The effects of different hydroxylation methods on the performances of devices were

investigated and compared. The results of X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) indicated clear evidences for the formation of strong dipoles across the interface between PEI and TiO<sub>2</sub> surface, which lead to the decrease of Schottky barrier height between Au and TiO<sub>2</sub>.

The chemical structure of PEI is shown in Fig. 1(a). In aqueous solution, the functional amines of PEI can be partially protonated by accepting protons (H<sup>+</sup>) dissociated from the water due to their strong basicity,<sup>21</sup> which makes PEI exhibit cationic characteristics. When PEI is deposited on the hydroxylated surface of TiO<sub>2</sub> from its aqueous solution, the electrostatic self-assembly of PEI occurs, as shown in Fig. 1(b) and 1(c). The positively charged amines (protonated amines) of the cationic PEI interact strongly with the negatively charged terminal oxygen ions of TiO<sub>2</sub> surface and then spontaneously alter the conformation of the polymer chains. The electrostatic interaction leads to an immediate and uniform formation of strong dipoles across the interface between PEI and TiO<sub>2</sub> surface. Consequently, the surface dipole moments pointing outwards from TiO<sub>2</sub> are opposite to the direction of built-in field in the space charge region, leading to the reduction of Schottky barrier height between Au and TiO<sub>2</sub>. The photocurrent of the device is improved thereby, which is responsible for the high photoresponsivity.<sup>22</sup>

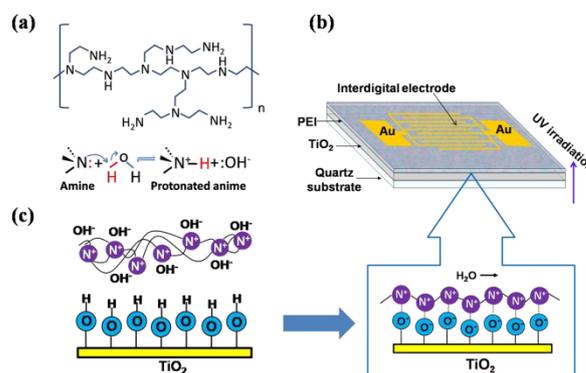


Fig. 1. (a) Chemical structures of the PEI. Schematic illustrations of (b) the MSM TiO<sub>2</sub> UVPD structure and (c) the electrostatic self-assembly of PEI on TiO<sub>2</sub> surface.

To support our analysis, surface analyses were performed using XPS on three cases, bare TiO<sub>2</sub>, UV/ozone treated TiO<sub>2</sub>/PEI

(TUP) and KOH treated TiO<sub>2</sub>/PEI (TKP). Fig. 2(a) and 2(b) shows the survey and high-resolution XPS spectra of the three cases. The survey XPS spectra of TUP and TKP clearly exhibit N1s peaks at a binding energy of 398.4 eV. For the high-resolution XPS spectra of TUP and TKP, there are two asymmetric N1s peaks centered at 398.6 eV and 400.1 eV. Because the two peaks can be assigned to the nitrogen atoms in the neutral amines and the protonated amines,<sup>21, 23–25</sup> respectively, the XPS spectra clearly demonstrate the existence of protonated amines at the surfaces of TiO<sub>2</sub>/PEI. In addition, it's worth noting that the intensity of N1s peak for TKP is larger than that of TUP. As the concentration of protonated amines on the TiO<sub>2</sub>/PEI surface determines the intensity of the electrostatic dipoles, it can be induced that stronger electrostatic self-assembly of PEI occurs on the surface of TiO<sub>2</sub> treated with KOH.

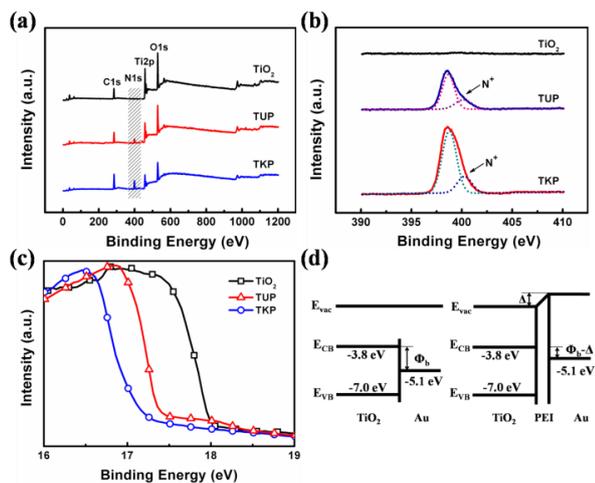


Fig. 2. (a) Survey XPS spectra and (b) high-resolution XPS spectra of N1s on the cases of TiO<sub>2</sub>, TUP, and TKP films. (c) UPS spectra on the surface of TiO<sub>2</sub>, TUP, and TKP. (d) Schematic energy diagrams of TiO<sub>2</sub>/Au (left) and TiO<sub>2</sub>/PEI/Au (right) constructed from the UPS spectra.

To clearly demonstrate the effects of PEI as an interfacial layer on Schottky barrier at TiO<sub>2</sub>/Au interface, UPS measurement was taken to determine the energy level alignment at the surface of TiO<sub>2</sub> modified by PEI. Fig. 2(c) shows the UPS spectra of bare TiO<sub>2</sub>, TKP, and TUP, the variation of second cut-off in the spectra indicates that the modification by PEI makes the vacuum level at TiO<sub>2</sub> surface shift up, and this shift can be attributed to the formation of interfacial dipoles ( $\Delta$ ) caused by the electrostatic self-assembly of PEI. The energy diagrams of TiO<sub>2</sub>/Au, and TiO<sub>2</sub>/PEI/Au extracted from the UPS spectra are shown in Fig. 2(d). It can be seen that the Schottky barrier, which is defined by the energy difference between the Fermi level of Au and the energy level of TiO<sub>2</sub> conduction band ( $E_{CB}$ ), is lowered from  $\Phi_b$  to  $\Phi_b - \Delta$  by the introduction of PEI. Subtracting the vacuum level of the bare TiO<sub>2</sub> from that of PEI-coated TiO<sub>2</sub> corresponds to the magnitude of the interfacial dipole. It can be calculated that the interfacial dipole  $\Delta$  of 0.94 eV is generated at TKP interface, larger than that of 0.60 eV at TUP interface. This suggests a larger reduction of Schottky barrier for the devices of TKP, which is accordant with the analysis of XPS spectra.

To explore the impacts of PEI on device performance, the current-voltage (I-V) characteristics of TiO<sub>2</sub> photodetectors with and without PEI are compared in Fig. 3(a), which were measured

in dark and under UV illumination at the wavelength of 310 nm with an 82.5  $\mu\text{W cm}^{-2}$  irradiation-intensity. The IV curves are plotted on a log-log scale to see them clearly. At 6 V bias, the device of bare TiO<sub>2</sub> gets the lowest photocurrent of 4.296  $\mu\text{A}$ , and the photocurrent is 48.189  $\mu\text{A}$  for the device of TUP. The highest photocurrent of 171.74  $\mu\text{A}$  is obtained for the device of TKP at the same condition, which is about 40 times higher than that for the device of bare TiO<sub>2</sub>. The dark current of the devices with and without PEI are almost the same, less than 5 nA at 6 V bias.

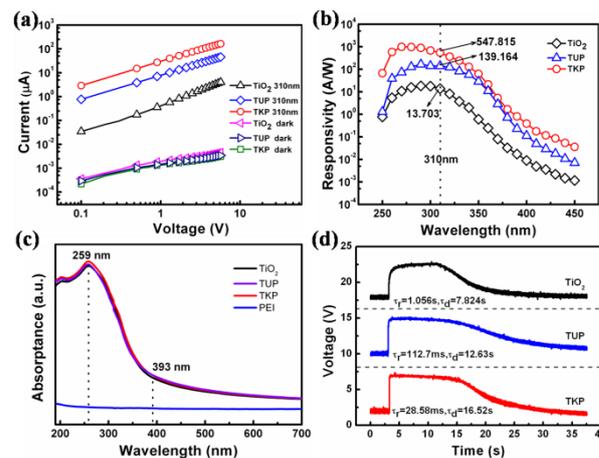


Fig. 3. (a) The typical I-V characteristics of the devices measured in dark and under 310 nm UV light illumination. (b) The spectral response of TiO<sub>2</sub>, TUP and TKP devices at 6 V bias. (c) The UV-Vis absorption spectrum of the as-prepared TiO<sub>2</sub>, TUP, TKP and PEI films. (d) The time response spectrum of TiO<sub>2</sub>, TUP, and TKP devices.

Moreover, the spectral photoresponse of the above devices at 6 V bias are also investigated [Fig. 3(b)]. It can be seen that the spectral photoresponse of the devices get a significant improvement at wavelength of 250-450 nm by the introduction of PEI, the device of TKP exhibits the best performance especially. However, it's worth noting that the response of all the devices decreased under the irradiation of shorter wavelength UV light, this may be attributed to the strong absorption of high-energy photons at or near the surface region of the semiconductor. The electron-hole pairs generated near the surface region typically have a lifetime shorter than those in the bulk, thus they contribute less to the photoresponse. In consequence, the response decreases in the shorter wavelength region.<sup>26</sup> To further investigate the sensitivity of the devices, the external quantum efficiency (EQE) spectrum for the three devices is also calculated (Fig. S1). The EQE of about 219,700% is obtained at the wavelength of 310 nm for TKP device by applying 6 V bias.

The UV-Vis absorption spectra of the as-prepared TiO<sub>2</sub>, TUP, TKP, and PEI films are shown in Fig. 3(c). The absorption of TUP and TKP are almost the same as that of the as-prepared TiO<sub>2</sub> film due to the negligible absorption of PEI in ultraviolet-visible and infrared regions. The response of the devices by applying the light from the top as well as the bottom are also investigated and compared. It's found that the response gets a significant decrease by applying the light from the top for both TUP and TKP devices (Fig. S2). This can be attributed to the resistance of incident light by Au electrodes, making the light not able to reach the junction. Therefore, the apparent improvement of photocurrent and photoresponse can be attributed to the lowered Schottky barrier

caused by the electrostatic self-assembly of PEI.

The time response characteristics of the devices upon switching light on and off are shown in Fig. 3(d). The response time of the device was obtained by measuring the voltage variation of a 5.1 M $\Omega$  load resistance in the test circuit. The rise time is 1.056 s for the device of bare TiO<sub>2</sub>, 112.7 ms for the device of TUP, and 28.58 ms for the device of TKP, respectively. The magnification image of the rise time region is shown in Fig. S3. The obvious decrease of the rise time is mainly attributed to the lowered and even thinner Schottky barrier, which facilitates the photo-induced charge transport between TiO<sub>2</sub> and Au electrodes. However, the fall time for the device of TKP is 16.52 s, about twice as much time as that for the device of bare TiO<sub>2</sub>. As shown in Fig. 2(d), the Fermi level of Au electrode is almost in the middle of the band gap of TiO<sub>2</sub> for the device without PEI. However, it is much closer to the conduction band of TiO<sub>2</sub> when the device is modified by PEI, and this will make Au electrodes harder to capture the holes when the generated electron-hole pairs reach the interface between Au and TiO<sub>2</sub>, leading to a significant reduction in the recombination rate of the carriers. In addition, because of the accordingly narrowed width of depletion region, both capacitance of depletion region and RC time constant are enlarged. The device capacitance (C<sub>d</sub>) at 1 kHz is 601 fF for the device of TUP. And C<sub>d</sub> is about 692 fF for the device of TKP, almost twice as that (368 fF) for the device of bare TiO<sub>2</sub>. Thus longer fall time is observed for the devices modified by PEI after turning off the light. The voltage can be reproducibly switched from the “on” state to the “off” state by periodically turning the light on and off (Fig. S4), indicating a good stability.

In summary, we have successfully demonstrated the high photocurrent, quick response MSM TiO<sub>2</sub> UVPDs using electrostatically self-assembled PEI as an interfacial layer. The Schottky barrier between Au electrodes and TiO<sub>2</sub> film is lowered by the modification of cationic PEI, which originates from the strong electrostatic self-assembled dipoles created by the presence of protonated amines at PEI/TiO<sub>2</sub> interface. Because the reduction of Schottky barrier facilitates the photo-induced charge transport between TiO<sub>2</sub> and Au electrodes, a very high photocurrent of 171.74  $\mu$ A at 6 V bias is obtained for the devices of TKP under the UV illumination, about 40 times as large as that (4.296  $\mu$ A) for the devices without PEI. The rise time of the devices is also shortened from 1.056 s to 28.58 ms.

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## Notes and references

<sup>a</sup> State Key Laboratory on Integrated Optoelectronics, Jilin University, 2699 Qianjin Street, Changchun 130012, People's Republic of China. E-mail: zhoujr@jlu.edu.cn

<sup>b</sup> College of Electronic Science and Engineering, Jilin University, 2699 Qianjin Street, Changchun 130012, People's Republic of China. E-mail: rsp1226@gmail.com

<sup>c</sup> School of Electrical, Computer and Energy Engineering, Arizona State University, Tempe, Arizona 85287, USA. E-mail: haifeng.zhang@asu.edu

† Electronic Supplementary Information (ESI) available: Experimental details, the photoresponse and EQE spectrum of the devices, rise time and electrical output under periodic light pulses. See DOI: 10.1039/b000000x/  
‡ These authors contributed equally to this work.

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