Analysis of optoelectronic properties of TiO_2 nanowiers/Si heterojunction arrays

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The optoelectronic properties of n-TiO_2NW/p-Si heterojunction fabricated by depositing TiO_2 nanowires on a p-Si substrate are studied. Under excitation at a wavelength of 370 nm, the TiO_2 nanowires produce a light emission at 435 nm due to the emission of free excitons. The *I*–*V* characteristics are measured to investigate the heterojunction effects under the dark environment and ultraviolet (UV) illumination. n-TiO_2NW/p-Si has a p–n junction formed in the n-TiO_2/p-Si heterojunction. TiO_2NW/Si photodiode produces a photocurrent larger than dark current under UV illumination. It is observed that UV photons are absorbed in TiO_2 and the heterojunction shows a 0.034-A/W responsivity at 4-V reverse bias.

Keywords: TiO_2 nanowires, photoresponse, *I*–*V* characteristics, heterojunction

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1. Introduction

TiO_2 is a wide band gap (3 eV–3.2 eV) semiconductor that has attracted considerable attention during the last decade. In particular, TiO_2 nanowires (NWs) have aroused noticeable interest for their various applications in gas sensors,[1] photocatalysis,[2–5] and solar cells.[6]

Semiconductor heterojunctions can absorb the solar spectra in different regions. The deposition of TiO_2 nanowires on p-Si structures means that n-TiO_2/p-Si heterojunction photodiodes can be synthesized, which are useful for improving the performance of photoelectric detectors. There are some reports on structures and optical properties rutile TiO_2 nanowires grown on Si substrate.[7–9] However, to date there have been few results concerning the heterojunction effect or the photodiode behavior of TiO_2 nanowires. Therefore, more studies in this field are necessary, especially in a nanostructure system. In 2011, Sai *et al.* reported reasonably large photocurrent-to-dark-current ratios and fast response P-Cu_2O-shell/n-TiO_2-nanowires-core photodiodes.[10] In 2012, Wang *et al.*[11] reported that n-TiO_2/C heterojunctions could increase absorption in the visible region and exhibit a higher photocatalytic activity.

In this research, n-TiO_2 nanowires on p-Si substrate are fabricated by thermal evaporation in horizontal furnace. The morphology, crystal structure, optical and electrical properties of this photodiode are investigated.

2. Experimental details

Using the thermal evaporation method, TiO_2 nanowires were successfully synthesized on p-type silicon as a substrate for the n-TiO_2/p-Si heterojunction. The substrate was ultrasonically cleaned in acetone and ethanol. A Ti buffer layer with a thickness of 20 nm was deposited on the substrate by the electron beam evaporation technique with an evaporation rate of 1.5 Å/s under a pressure of 10^{-5} mbar (1 bar = 10^5 Pa). A gold film with a thickness of 3 nm was deposited as a catalyst on the Ti layer by a sputtering system. The substrate was placed on a quartz boat in the zone with a temperature of 850 °C while the mixture of Ti and graphite powder was placed in the middle of a horizontal quartz furnace as the source material. The heating ramp was 20 °C/min up to 1050 °C and this was held for 1 h. Then, the substrate cooled down to room temperature. The substrate was then taken out for characterization. To provide a lower contact resistance of the electrode, a 0.5-mm-diameter Ag dot of circle form was contacted onto a TiO_2 surface. In the same manner, a contact was made onto the backside of the Si wafers. The *I*–*V* characteristics were measured in air at room temperature by changing voltage from −4 V to +4 V in the dark environment and under illumination light, respectively.

The structures and morphologies of the samples were analyzed by field emission scanning electron microscope (FE-SEM: S-4166, Hitachi) and X-Ray diffraction (XRD: JEOL JDX-8030). The photoluminescence (PL) spectra of the samples were recorded with a Cary Eclipse spectrophotometer at room temperature under excitation of 370 nm. The photo *I*–*V* characteristics were measured under illumination by Melles Griot He–Cd Laser (Series 56) with an intensity of 4 mW at a 325-nm wavelength.

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3. Results and discussion

3.1. Morphological and crystallographic properties

Top view scanning electron microscope (SEM) analysis is used to investigate the morphology of TiO_2 nanowires. Figure 1 shows nanowires with diameters of around 40 nm–100 nm and lengths of about 500 nm–1000 nm.

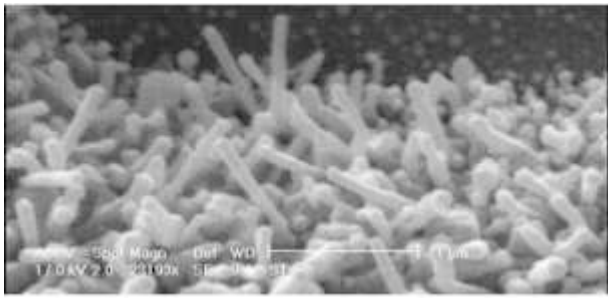


Fig. 1. SEM images of as-synthesized TiO_2 nanowires by thermal evaporation. Scale bar is 1 μm.

Table 1. Calculated values of lattice constants and texture coefficient.

Sample	a/Å	c/Å	TC/(110)	TC/(101)	TC/(211)
TiO_2 nanowires	4.59	2.95	0.92	1.36	0.68

To study the crystal structure of TiO_2 nanowires, an X-ray diffraction (XRD) experiment was performed. Figure 2 shows XRD patterns for TiO_2 nanowires. The peaks at 27.4, 36.1, 44.29, 54.3, and 56.6 correspond to reflections from (110), (101), (111), (211), and (220) crystal planes of rutile TiO_2, respectively. The calculated unit cell constants from XRD patterns, shown in Table 1, are in good agreement with the standard data ((JCPDS: 73–1765, $a = 4.52$ Å, $c = 2.98$ Å). In order to study the orientation of TiO_2 nanowires, texture coefficient TC (hkl) three higher diffraction peaks at (110), (101), and (211) are calculated and listed in Table 1. The texture coefficient TC is calculated by using the following formula:[12]

$$TC(hkl) = \frac{I_{(hkl)}/I_{0(hkl)}}{N^{-1}\Sigma_N I_{(hkl)}/I_{0(hkl)}}, \quad (1)$$

where, $I_{(hkl)}$ is the measured intensity, $I_{0(hkl)}$ is the standard intensity of (hkl) plane taken from the JCPDS data, and N is the total number of diffraction peaks. If TC is equal to 1, then a sample with random orientations exists, while for a value larger than 1 a preferred orientation exists along the (hkl) plane. The calculated values of TC (hkl), shown in Table 1, indicate that (101) is the preferred direction, which is accordant with the result from the XRD patterns.

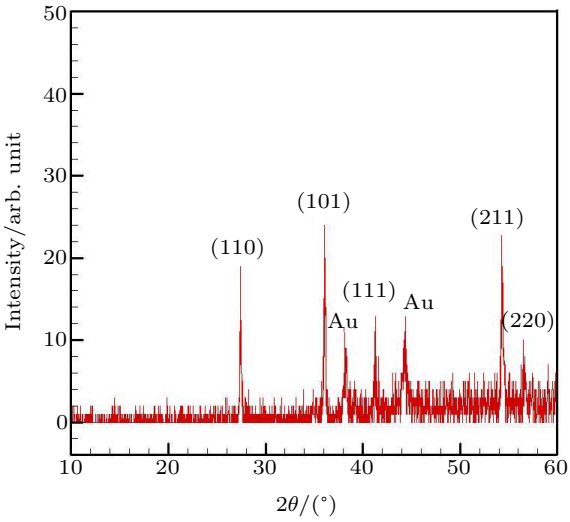


Fig. 2. (color online) XRD pattern of TiO_2 nanowires.

3.2. Optical properties

Figure 3 shows the photoluminescence emission spectrum of TiO_2 nanowires at room temperature under excitation at a wavelength of 370 nm. We can see a major peak at 435 nm and three week peaks at 486, 506, and 541 nm. The origins of a major peak and three week peaks can be attributed to the emission of free excitions and the oxygen vacancies of defect centers at the surface of TiO_2 nanowires, respectively.[13,14]

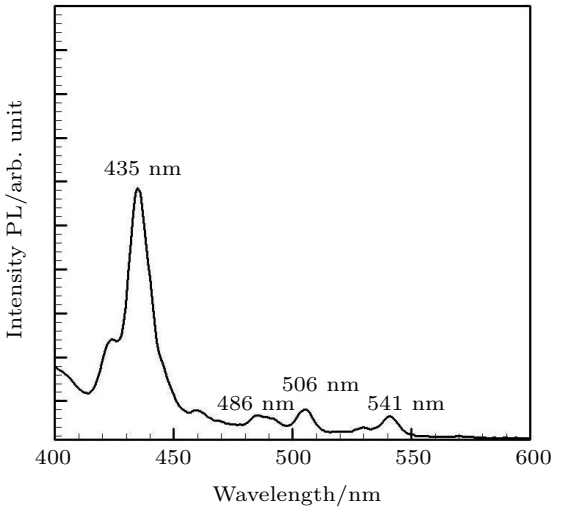


Fig. 3. Room temperature PL spectra of TiO_2 nanowires. Excitation wavelength is 370 nm.

3.3. Electrical properties

In order to study the electrical properties, I–V characteristic curves of TiO_2 nanowires are measured in the dark environment and under ultraviolet (UV) illumination respectively. During the photo-response measurements, a 325-nm He–Cd laser with an intensity of 4 mW is used as an excitation source. Figure 4 shows a schematic illustration of the device and I–V

characteristic curves in the dark environment and UV illumination by changing the bias voltage from −4 V to +4 V. The rectified current characteristic is observed in the dark environment from a p–n junction at a forward bias. In this case, the turn-on voltage is 1.6 V. As shown in Fig. 4, under forward bias conditions the photocurrent is higher than the dark current. Under forward bias, the turn-on voltage is approximately 1.2 V. The photocurrent is given by

$$I_{\rm ph} = I_{\rm illuminated} - I_{\rm d}, \tag{2}$$

where $I_{\rm d}$ is the dark current and $I_{\rm illuminated}$ is current under illumination. The photocurrent is 1.5 times higher than that in the dark environment at 4 V. The operation of the photodiode detector involves three steps, which are: (i) the generation of electron–hole pairs by absorbing incident light; (ii) the separation and transport of (e–h) pairs by the internal electric field; and, (iii) the interaction of current with the external circuit to generate an output signal. When a heterojunction, which is formed by the deposition of a wide band gap semiconductor (TiO_2) on narrow band gap (Si), is illuminated under UV light, the UV light can be absorbed by TiO_2 and electron–hole pairs are produced by TiO_2. In this process, the photogenerated electrons in TiO_2 nanowires move towards the surface, while the photogenerated holes in TiO_2 nanowires move to the p-Si in p–n junction. Consequently, a net photocurrent is generated.

The photoresponsivity of TiO_2/Si heterojunction is expressed as $R = I_{\rm ph}/P_0$,[14] where $I_{\rm ph}$ is the photocurrent and P_0 is the optical power at a wavelength. The responsivity of our heterojunction is given to be 0.034 A/W at −4 V, which is in accordance with that reported by Chang *et al.*[15]

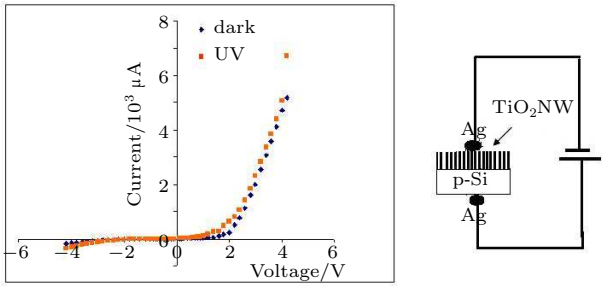


Fig. 4. (color online) *I–V* characteristics of n-TiO_2NW/p-Si heterojunction in the dark environment and under UV light. The right panel shows schematic illustration of TiO_2 nanowires under forward bias.

Figure 5 shows the dynamic photoresponse measured under −4 V applied bias. In the dark environment, the leakage current is 4.2×10^2 μA. When the sample is illuminated by UV light, the leakage current increases to 1.52×10^3 μA. The rise and decay time constants calculated from curve in Fig. 5 are 40 s and 70 s. The large time constants show a delay on the rising part and a delay on the falling part of the photocurrent, which is due to the absorption/desorption of oxygen molecules on the nanowire's surface.[14]

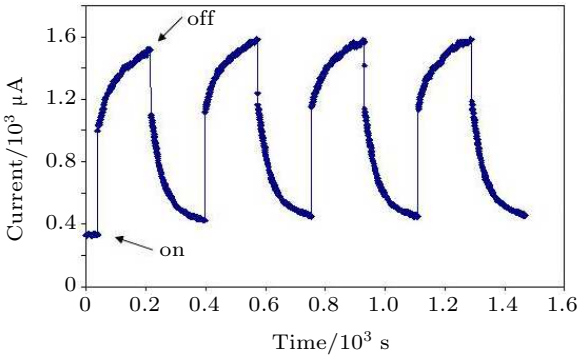


Fig. 5. (color online) Light response for n-TiO_2NW/p-Si heterojunction under reverse bias.

4. Conclusions

An n-TiO_2/p-Si heterojunction is fabricated by depositing TiO_2 nanowires on p-Si substrate. The calculated value of TC (hkl) indicates that (101) is the preferred direction. The *I–V* characteristics in the dark environment and UV illumination indicate that the photocurrent is 1.5 times higher than that in the dark environment, at 4 V.

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