Solar-Blind Photodetector Based on NaTaO$_3$/TiO$_2$ Composite Film with Enhanced Photoelectric Performance

Min Zhang, Zhenjiang Li, Yunfei Zhao, Zhaofeng Wu *, Jun Zhang *, Linyu Yang, Shuying Wang and Shiqing Li

Xinjiang Key Laboratory of Solid State Physics and Devices, School of Physics and Technology, Xinjiang University, Urumqi 830046, China; minzhang0816@163.com (M.Z.); zhenjiangli1210@163.com (Z.L.); zhaoyf@foxmail.com (Y.Z.); yanglinyu0222@ sina.com (L.Y.); wsymlerr@sina.com (S.W.);
lishiqingdsg66@163.com (S.L.)
* Correspondence: wuzf@xju.edu.cn (Z.W.); zhj@xju.edu.cn (J.Z.)

Abstract: In this study, ultraviolet detectors based on NaTaO$_3$/TiO$_2$ were fabricated with enhanced detection performance towards solar-blind (200–280 nm) light. A TiO$_2$ seed layer was introduced and served as a buffer layer between the fluorine tin oxide (FTO)-coated glass substrate and the TiO$_2$ film, which increased the adhesion between them. The periodic stability and photoelectric characteristics of the detectors were studied and analyzed. The detectors showed a high performance when illuminated by 265 nm and 254 nm UV light. At $-15$ V bias, the dark current of the detector was only 70 pA. Under the bias of $-15$ V and the illumination of 254 nm, the maximum photo-to-dark current ratio reached 20, and the response time was less than 300 ms. Moreover, the detector exhibited a fast response time and remained very stable after numerous testing cycles. These results demonstrate the potential application of NaTaO$_3$/TiO$_2$ composites in UV detection.

Keywords: NaTaO$_3$; TiO$_2$; composite film; isotype heterojunction; solar-blind detector

1. Introduction

UV (Ultraviolet) detection has attracted considerable attention and has been applied in monitoring ozone holes, flame detection, space communication, missile guidance, and UV disinfection. UV light emitted by the sun is the most important source of natural UV radiation. However, the solar-blind area with wavelengths from 200–280 nm is mainly absorbed by diatomic oxygen or ozone. Therefore, the term “solar-blind” refers to the UV region that can be detected without the influence of atmospheric background noise [1]. The substrate materials of solar-blind detectors generally adopt wide band-gap semiconductors, such as Zn$_x$Mg$_{1-x}$O, Al$_x$Ga$_{1-x}$N, Ga$_2$O$_3$ or SiC. However, the application of these materials in solar-blind UV detection is more or less limited. Metal oxide semiconductors, such as Zn$_x$Mg$_{1-x}$O, Al$_x$Ga$_{1-x}$N, and Ga$_2$O$_3$, are challenging to achieve p-type doping [2–4]. On the other hand, the preparation of SiC usually requires a high temperature [5,6]. Thus, we proposed simple and easily available semiconductors to fabricate solar-blind detectors. TiO$_2$ is widely used in the manufacture of UVA (320–380 nm) detectors. Moreover, there are few reports about NaTaO$_3$ as a solar-blind detector. Some organic–inorganic hybrid UV detectors based on NaTaO$_3$ (excited by 260 nm UV light) have excellent comprehensive performance, such as high sensitivity and fast response speed. However, the detectors are faced with the problem of UV degradation during their work, which may lead to unstable detection performance [7]. Zhang et al. firstly reported an MSM (metal–semiconductor–metal) detector based on NaTaO$_3$ (excited by 260 nm UV light). However, the response time of the device was too long, and the photoelectric sensitivity was also relatively low [8,9]. Therefore, it is considered worthy to combine the advantages of TiO$_2$ and NaTaO$_3$ by employing the heterojunction device structure to fabricate low-cost and easily obtainable solar-blind detectors. Based on the previously mentioned aspects, it can be
supposed that this kind of detector could have good stability, low response times, and high photoelectric sensitivity.

As a potential candidate, the perovskite-type NaTaO$_3$ is sensitive toward UV light because of its relatively wide band-gap (4.0 eV) and high UV activity [10,11]. Furthermore, NaTaO$_3$ can be synthesized using low-cost approaches, such as the hydrothermal/solvothermal methods [12,13] or the sol–gel process [14–16]. In this study, solar-blind detectors based on NaTaO$_3$/TiO$_2$ with silver electrodes were fabricated, and their photoelectric characteristics were investigated in detail. Here, a TiO$_2$ seed layer was also introduced to strengthen the coupling between the device substrate and TiO$_2$ film. The NaTaO$_3$ film acts as a UV photosensitive layer, whereas the TiO$_2$ film works as an electron transport layer. Moreover, these components could form a heterojunction structure. Furthermore, it was found that the NaTaO$_3$/TiO$_2$ detector demonstrates excellent solar-blind detection performance as compared to single component-based devices.

2. Experiment

The reagents used in this experiment were provided by Aladdin (Shanghai, China), with analytical reagent (AR) grade purity. The deionized water was made in the laboratory. All the reagents were used without further purification.

The preparation of TiO$_2$ sol–gel for the seed layer included the dissolution of 1 mL tetrabutyl titanate [Ti(OC$_4$H$_9$)$_4$] in 6 mL of ethanol, after stirring until the end. Then, 1 mL acetylacetone was added into the mixed liquid. Subsequently, 3 mL of ethanol and 1 mL deionized water were added to the mixture. After that, 1 mL of glacial acetic acid was dripped in the solution. The mixture was stirred at room temperature for at least 24 h to obtain the TiO$_2$ sol–gel solution.

The fluorine tin oxide (FTO)-coated glass substrate was cleaned with acetone, ethanol, and deionized water, respectively. To prepare the TiO$_2$ seed layer on the substrate, the above-prepared TiO$_2$ solution was directly spin-coated on FTO at a rate of 3000 rpm for 12 s to ensure uniformity. Part of the FTO was covered by polyimide tape to prevent it from being entirely covered by the TiO$_2$ solution. Next, the sample was annealed at 500 °C for 1 h. For the synthesis of TiO$_2$ film, the TiO$_2$ seed layer/FTO was immersed into Teflon-lined stainless-steel autoclaves (50 ml, Kori, Gongyi, China) with a capacity of 23 mL. The autoclaves contained 10 mL of toluene, 1 mL of Ti(OC$_4$H$_9$)$_4$, 0.2 mL of titanium tetrachloride, and 1 mL of hydrochloric acid. The autoclaves were sealed and kept at 180 °C for 2 h and then naturally cooled to room temperature. The films were dried in the air at room temperature.

For the fabrication of the NaTO$_3$ layer, hydrothermal treatment was applied to synthesize the microcubes: 2.4 g NaOH and 0.884 g Ta$_2$O$_5$ were dispersed in an 80 mL mixed solution, which contained deionized water and ethylene glycol (EG) with a volume ratio of 20:60. After magnetic stirring (DF-101S, Kori, Gongyi, China) for 2 h, the mixed solution was transferred into a 100 mL autoclave and heat-treated at 150 °C for 12 h. Finally, the samples were separated by centrifuging (TD6M, JTLIANGYOU, Changzhou, China) and dried at 80 °C in an oven for 5 h. Next, ethyl celluloses with different viscosities (9–11 MPa·s and 45–55 MPa·s) were mixed at a mass ratio of 40:60. The ethylcellulose mentioned above was dispersed in ethanol to prepare a 20 wt% suspension. After that, the prepared NaTO$_3$, ethylcellulose suspension, and terpineol with appropriate ratios were ground in a mortar for 2 h. The solution was spin-coated on TiO$_2$ film at a rate of 5000 rpm for 12 s to ensure uniformity. The as-obtained composite film was then annealed at 500 °C for 1 h. The flow chart of the synthesis pathway is presented in Figure 1.

The crystal structure of the samples was examined by X-ray diffraction (XRD) on a D8 Advance of Bruker AXS GmbH (Karlsruhe, Germany). The optical characterization of the films was examined by a Lambda 650 S UV/VIS spectrometer of Perkin-Elmer (Waltham, MA, USA). The morphology of the samples was observed using a scanning electron microscope (SEM) (ZEISS sigma500, Jena, Germany; Energy spectrum: BRUKER XFlash 6130, Suwon, Korea). The I-V characteristics and time response of the devices under
UV light irradiation were measured by an Electrochemical Workstation (Zennium pro, Kronach, Germany). The UV light irradiation was calibrated by the radiometer (LS125 using by UVC LED probe, LinShang, Shenzhen, China).

3. Results and Discussion

3.1. Structure Analysis

The crystalline phase of the composite film was characterized by the XRD analysis, shown in Figure 2. The composite film contained both NaTaO$_3$ (JCPDS card #25-0863) and TiO$_2$ (JCPDS card #99-0090) components. Compared with the standard PDF cards, NaTaO$_3$ and TiO$_2$ exhibited a perovskite-like and rutile structure, respectively. The narrow and sharp diffraction peaks showed good crystallinity of the samples. For the composite film, there was a strong diffraction peak at 62.8°, which was assigned to the (002) crystal plane of TiO$_2$ [17]. The diffraction peaks found at 22.9° and 32.5° were assigned to the NaTaO$_3$. The space group of the NaTaO$_3$ component belongs to P4/mbm [18,19], which is a typical structure of perovskite and has good phase stability. Except for TiO$_2$ and NaTaO$_3$, the rest of the diffraction peaks originated from the FTO substrate (SnO$_2$, JCPDS card #99-0024).

3.2. Morphology Analysis

In Figure 3a, it can be seen that the TiO$_2$ film showed a dense morphology. Figure 3b shows a typical morphology of the NaTaO$_3$ sample prepared by the hydrothermal method (before the heat treatment). In general, the grains still maintained their cubic shape, but the
corners became less sharp. Moreover, the morphology of the grains was in the transition between cube and sphere, according to previous research [20]. Figure 3c shows the cross-section image of the composite film after heat treatment. The separation between different interfaces is pronounced, and the composite film is very uniform with a thickness of about tens of microns. The NaTaO₃ grains, as shown in Figure 3b, are grown and annexed to form a well-covered NaTaO₃ film (shown in Figure 3c) through a powder metallurgy process. As the TiO₂ layer is very thin, the interface between TiO₂ and NaTaO₃ is not clearly observable. Furthermore, different film layers were connected due to the diffusion after heat treatment, which is consistent with the results displayed in the previous report [21].

Figure 3. SEM images of (a) the top view of the TiO₂ film; (b) pure NaTaO₃ crystal samples prepared by hydrothermal method before heat treatment. (c) The cross-section image of the composite film.

3.3. Absorption Spectrum and Device Structure

Figure 4a displays the absorption spectra of pure NaTaO₃, TiO₂, and the NaTaO₃/TiO₂ composite film. In the case of the TiO₂ layer, the UV light easily penetrated the thin film due to the optical tunneling effect, resulting in a weak absorption of UV light (Figure 4a). Meanwhile, the surface of TiO₂ film was uneven, as shown in Figure 3a. According to light’s coherence, there is an extinction effect when the height difference reaches about a quarter of the light wave. In the range of less than 320 nm, the absorption values of the TiO₂ layer increased. When NaTaO₃ and TiO₂ were combined, the good UV absorption of NaTaO₃ and the reduced light penetration by the multilayer films both contributed to the high UV absorption of NaTaO₃/TiO₂ composite. Therefore, the composite film showed high absorption values. According to the Lambert–Beer law, the absorbance of each component could superimpose over one another at the same wavelength. Therefore, the two peaks of the composite film, located around 285 nm, were from the two components’ superposition. The other one in the range of 330–380 nm should be mainly from TiO₂.

Figure 4. (a) The absorption spectrum of pure NaTaO₃, TiO₂ and the NaTaO₃/TiO₂ composite film; (b,c) the device structure diagram of the composite-film-based detector.
Figure 4b,c clearly shows the structure of the composite film. The TiO$_2$ section is composed of two layers: the TiO$_2$ film and the bottom TiO$_2$ seed layer. The latter was used to strengthen the connection between the upper TiO$_2$ film and the substrate. The composite film was obtained by covering a NaTaO$_3$ layer on the TiO$_2$ film. Then, one silver electrode was drawn from the conductive surface of the FTO glass and the other one was led out from the composite film. In addition, the surface of the silver electrode easily formed an oxide layer, especially when the silver electrodes were heat-treated at 60 °C after the deposition process. In this situation, the Schottky effect between metal and semiconductors could be ignored. The I-V characteristics were tested by applying a reverse bias, with NaTaO$_3$ as the anode and TiO$_2$ as the cathode.

3.4. I–T and I–V Characteristics

Figure 5a shows the time-dependent photocurrent response of the pure NaTaO$_3$ and the composite-film-based devices under different UV irradiations at −15 V bias. Compared with the composite-film-based detectors, the pure NaTaO$_3$ device showed a poor performance towards solar-blind light detection, showing a photo-to-dark current ratio of only three. The NaTaO$_3$/TiO$_2$ detectors displayed a much lower photocurrent under 285 nm UV light. Their photocurrent reached the maximum when the 254 nm UV light illuminated the devices. At the same applied bias, the dark current of the detector was about 70 pA, indicating a low noise and power consumption of the device. After multiple testing cycles, the detectors maintained stable performance, and the response speed changed very rapidly with the light on and off. The response time was less than 300 ms. Additionally, a TiO$_2$ detector was also fabricated for comparison, displaying a weak response to solar-blind light. Figure 5b shows the I–V characteristics of the NaTaO$_3$/TiO$_2$-based detector in the dark and under illumination. The I–V curves display prominent non-linear characteristics. In addition, the device barely responded to 285 nm UV illumination, and the corresponding photo-to-dark current ratio was negligible. Under the bias of −15 V and 254 nm, the maximum photo-to-dark current ratio reached 20.

For n-N heterojunction in this study, a potential barrier was produced by the electron concentration difference on both sides, and the electron concentration was high. Therefore, in n-N typed heterojunction, the barrier is easily disturbed from the outside. The accumulation layer of n-N heterojunction is thin. When high-energy photons were injected continuously, the photo-generated carriers drifted and diffused, to break the original balance, and reduce the electron concentration difference on both sides, leading to the decrease in barrier height; the higher the photon energy, the greater the influence on the potential barrier. Thus, compared with the I–V characteristic curve in the dark, the minimum
current point moved to the left under illumination conditions with wavelength decreases. Therefore, an opposite behavior to the p-n junction was observed.

Table 1 shows the responsivity of the NaTaO$_3$/TiO$_2$-based detectors under different UV illumination. To investigate the response of the current to the incident optical power, the responsivity ($R_\lambda$) was calculated using the Equation (1):

$$R_\lambda = (I_\lambda - I_d) / P_\lambda \times S$$  \hspace{1cm} (1)

where $I_\lambda$ is the photocurrent, $I_d$ is the dark current, $P_\lambda$ is the light intensity, and $S$ is the illuminated area (the area of the composite film device was 1 cm$^2$) [22]. Compared with some previously reported solar-blind UV detectors, our devices show a comparable response [23,24].

Table 1. The responsivity of the NaTaO$_3$/TiO$_2$-based detectors under different UV illumination.

| Wavelength (nm) | Light Intensity (mW/cm$^2$) | Responsivity (mA/W) |
|-----------------|-----------------------------|---------------------|
| 254             | 1.02                        | 1.29                |
| 265             | 0.52                        | 1.65                |
| 275             | 0.43                        | 0.22                |
| 285             | 0.01                        | 0.01                |

3.5. Analysis

The intrinsic defects of rutile TiO$_2$, such as Ti$_i$, interstitial titanium atoms, or V$_O$ (oxygen vacancy), played the role of shallow donors. Therefore, TiO$_2$ usually presents the properties of an n-type semiconductor [25–27]. According to the first principle calculation, NaTaO$_3$ usually behaves as an n-type semiconductor [28]. After annealing in a non-oxygen enriched environment, the experimental results also proved this point [29]. Therefore, isotype heterojunction formed at the NaTaO$_3$ and TiO$_2$ contact interface. In the growth of polycrystalline films, a large number of defects were inevitable. As a result, a severe scattering effect could be observed on the carriers’ transport, causing a low conductivity.

According to the calculation simulation of TiO$_2$ and NaTaO$_3$ [30,31], the contribution to the space charges of carriers (holes) could be ignored, and the electrons obeyed the Boltzmann statistical distribution. The band diagram of the n-N heterojunction was approximately processed by the Poisson equation, as shown in Figure 6 [25,32–36]. The bandgap of TiO$_2$ is 3.0 eV, that of NaTaO$_3$ is 4.0 eV [37]. The barrier decreased mainly on the low carriers’ region, and the wide-band semiconductor side was basically depleted. The barrier height on the narrow-band semiconductor side held a small proportion in the whole. According to the first-principle calculations [29,30], the current under reverse bias, which is unsaturated, is determined by the electron transfer in the narrow-band semiconductor. Since this barrier height is relatively small, the barrier would be flattened whenever a small voltage is applied, leading to a non-rectifying characteristic of the detector. This theoretical analysis was in good agreement with the non-linear curves presented by the I-V characteristics of the device.

![Figure 6](image_url)  \hspace{1cm} Figure 6. The energy band schematic diagrams of NaTaO$_3$/TiO$_2$: (a) in dark (b) under UV light.
In the n-N heterojunction, the potential barrier mainly appears in the conduction band. When there is no light, at the contact interface, the TiO$_2$ conduction band tends to be concave due to the potential well [36]. When photons with enough energy are injected, more electrons in the valence band are excited and enter the conduction band. Due to the fact that the potential well is small and easy to fill, Figure 6a,b shows manifest differences [34]. As is presented by some research, the photo-response of UV detectors mainly hinges on the lifetime and quantity of photo-generated carriers [38]. The mechanism of the enhanced response of the NaTaO$_3$/TiO$_2$ heterojunction-based detector can be better understood through the band structure diagrams in Figure 6. Since the energy barrier exists between the conduction bands of TiO$_2$ and NaTaO$_3$ [37], the excited carriers would transfer easily between NaTaO$_3$ and TiO$_2$. When the composite film is irradiated by UV light, photo-generated electrons are separated rapidly by the heterojunction interface, leading to a high density of carriers in TiO$_2$. It is reasonably speculated that the heterostructure formed at the NaTaO$_3$/TiO$_2$ interface can reduce the recombination probability between photo-generated carriers and prolong their lifetime. As a result, a remarkable photocurrent improvement is obtained.

4. Conclusions

In conclusion, the NaTaO$_3$/TiO$_2$ heterojunction was successfully synthesized by spin coating NaTaO$_3$ on the TiO$_2$ film. The UV detector was fabricated by depositing silver electrodes on the composite film surface. Then, UV photoelectric properties of NaTaO$_3$/TiO$_2$ heterojunction were investigated. At −15 V reverse bias, the detector’s dark current was about 70 pA, and a photo-response peak of 1.65 mA/W was obtained under the irradiation of 265 nm UV light. The photocurrent was 20 times larger than the dark current, indicating that the device has potential applicability in solar-blind UV light detection. The single TiO$_2$ film-based detector did not show a photo-response to UV light. The photo-to-dark current ratio of the pure NaTaO$_3$-based detector was only 3, which was much lower than that of the NaTaO$_3$/TiO$_2$-based device. The response mechanism of the composite detector under UV light was also discussed in detail. The heterostructure of the NaTaO$_3$/TiO$_2$ interface would reduce the recombination probability between photo-generated carriers; therefore, the increased carrier lifetime contributes a lot to the photo-response of detectors.

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