Phototransistor Based on Single TaON Nanobelt and Its
Photoresponse from Ultraviolet to Near-infrared

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Abstract: TaON nanobelts (NBs) were controllably synthesized by Ta2O5 NBs template-conversion method. The typical NBs have cross-sections of 40 nm×200 nm–400 nm×5600 nm, and lengths up to about 0.5 cm. A field effect transistor (FET) based on single TaON NB was fabricated on SiO2/Si substrate. The electronic mobility and on-off ratio of the nanobelts are 9.53×10⁻⁴ cm²/(V·s) and 3.4, respectively. The FET shows good photoresponses from 254 nm to 850 nm. Under irradiation of 405 nm light (42 mW/cm²), the responsivity is 249 mA/W at a bias of 5.0 V, and the photoswitch current ratio is 11. Therefore, the phototransistor shows a good photodetectivity, and TaON NBs may become good candidates for fabricating optoelectronic devices. Additionally, Ta2O5@TaON composite NBs were also synthesized, and a FET based on the single NB was fabricated. Under irradiation of the same light, its photoresponse is weaker than TaON NB, but it is still a good optoelectronic material.

Key words: TaON nanobelt; template synthesis; field effect transistor; photodetector

One-dimensional (1D) nanostructures of semiconductors have extensively been applied as functional building blocks for electronic and optoelectronic devices such as field-effect-transistors (FETs)[1], chemical sensors[2], electronic field emitters[3-4], photodetectors[5-7], solar cells[8], and supercapacitors[9], because the reduced dimensionality brings about new physical-chemical properties, and 1D nanostructures are suitable for nanofabrication. Research shows that the high photoconductive gains of the low dimensional semiconductor photodetectors depend on both their high surface-area-to-volume ratios (SVRs) and the reduced dimension of the effective conductive channel, because the high SVRs can increase the number of surface trap states and prolong photocarrier lifetime, whereas the reduced dimensionality can confine the active area of the charge carrier, and shorten the transit time[10]. Photodetector from the ultraviolet (UV) to the infrared (IR) is critical for industrial and scientific applications such as images sensing, communications, environmental monitoring, remote control, day-and-night-time surveillance, and chemical/biological sensing[11]. Although a few photodetectors based on nanostructures of metal oxides[12-13], metal chalcogenides[14], transition metal dichalcogenides (TMDs)[15-16], and transition metal trichalcogenides (TMTs)[17-18], are reported, it is still a challenge to develop low-cost, nontoxic, high-detectivity and broadband response photodetector.

TaON is a semiconductor with a band gap of 2.4 eV[19]. Its powders were once proposed as a nontoxic yellow pigment[20]. Recently, they have been used as visible-light-driven photocatalysts to split water[21] and oxidize methanol[22]. TaON powders could be prepared by calcination of Ta2O5 powders in the flowing NH3, for example, Ta2O5 could be totally converted to TaON in the flowing NH3 of 10 mL/min at 800 °C for 10 h, while totally converted to Ta3N5 in a flowing NH3 of 1000 mL/min at 800 °C for 10 h[23]. We once synthesized Ta3N5 nanobelts (NBs) by direct aminolysis of TaS3 NBs at high temperature, and discovered its good photosensitive properties from 250 nm to 630 nm[24]. In order to develop new photosensitive materials, here a Ta2O5 NB template conversion method was employed to synthesize TaON NBs, and reaction time was reduced to 3 h. Phototransistor based on single TaON NB shows good photoresponse from ultraviolet (UV) to near infrared (NIR), and have higher photoswitch current ratio (PCR) than Ta3N5 NB photodetector[24].
1 Experiment

1.1 Preparation of TaON nanobelts

Firstly, TaS\(_3\) NBs were prepared by chemical vapor transport method\[^{[25-26]}\]. In typical process, 825 mg of tantalum (Ta) foil (99.9%, 0.2 mm×35 mm×45 mm), 146 mg of sulfur (S) powders (99.99%), and 15 mg of iodine (I\(_2\)) powders (99.8%) were sealed in a quartz ampoule in vacuum (ϕ0.6 cm×12 cm, ca. 10\(^{-2}\) Pa). The Ta foils were adjusted at the center of the ampoule and then the ampoule was placed at the center of a conventional horizontal furnace (ϕ4 cm×32 cm) with a temperature gradient of ca. 10 °C/cm from center to end. Then the furnace was heated to 550 °C at a rate of 10 °C/min, kept at 550 °C for 8 h, and cooled naturally to room temperature. TaS\(_3\) NBs on the Ta foils were extracted from the ampoule.

Secondly, TaS\(_3\) NBs were directly oxidized into Ta\(_2\)O\(_5\) NBs at 650 °C for 2 h in air.

Finally, the Ta\(_2\)O\(_5\) NBs were transferred into quartz coat, and placed in the center of the quartz tube of the horizontal furnace, then converted into green-yellow TaON NBs at 850 °C for 3 h in the flowing atmosphere of Ar (20 mL/min)/NH\(_3\) (80 mL/min) with a rising temperature rate of 10 °C/min.

1.2 Characterization

The products were characterized by X-ray diffractometer (XRD) under monochromatized Cu Ka-radiation (Shimadzu XRD-6000), LEO-1530VP scanning electron microscope (SEM), JEOL-JEM-2010 high-resolution electron microscope (HRTEM) using imaging and selected area electron diffraction (SAED) with an energy dispersive X-ray spectrometer (EDX). The UV-Vis absorbance spectra of the products were recorded by UV-3600 spectrophotometer (Shimadzu UV-3600).

1.3 Device fabrication and measurements

To fabricate field-effect-transistor (FET) of single NB, the TaON NBs were suspended in ethanol by brief sonication and then deposited on Si substrate with 300 nm thick thermal oxide layer serving as gate oxide. The standard photolithography technique followed by Ti/Au (10 nm/100 nm) metal evaporation and lift off were used to define the source and drain electrodes electrically contacting the NBs. The current-voltage (I-V) and current-time (I-t) characteristics of the photodetector were measured by SM-4 probe system and Keithley 236 source meter. The spectroscopic response ranging from 350 nm to 900 nm was measured using a 300 W Xe lamp (HSXUV300), and a multi-grating monochromator (71SW151) with ordered sorting filters. Small Lasers and ultraviolet lights were also used. Optical powers were measured with FZ-A, UV-340B, and UV-B radiometers. All measurements were carried out in air at room temperature.

2 Results and discussion

Fig. 1(a) shows the XRD pattern of as-prepared TaON NBs, which can be completely indexed as a monoclinic phase of TaON (JCPDS 71-0178). Fig. 1(b,c) display the low- and high-magnification SEM images of the NBs, respectively, revealing that the typical NBs have a rectangular section of about 40 nm×200 nm–400 nm×5600 nm, and a length up to 0.5 cm. Inset is the photography of NBs, showing faint yellow. Fig. 1(d) exhibits TEM image of single TaON NB, and inset shows the corresponding HRTEM image. The lattice fringe space of 0.31 nm corresponds to the (111) plane of TaON. Fast Fourier transform (FFT) pattern of the HRTEM image (inset on the upper right corner) further confirms it is monoclinic TaON. To probe for synthetic condition of pure TaON NBs, the same experiments were carried out at different temperatures. If TaO\(_2\) NBs were calcined at 650 °C for 3 h, the products were still TaO\(_2\). If TaO\(_2\) NBs were calcined at 750 °C for 3 h, only TaO\(_2\)@TaON composite NBs were synthesized. Fig. 2(a) is XRD pattern of the product at 750 °C, indicating mixture of TaO\(_2\) (JCPDS 71-0639) and TaON (JCPDS 71-0178). Fig. 2(b) is SEM image of the composite NBs, revealing that the nanobelts are still a rectangular section of 40 nm×200 nm–400 nm×5600 nm and a length up to 0.5 cm. Inset is a photography of the NBs with faint yellow. Fig. 2(c) displays TEM image of the composite NBs. TEM image of a single NB (Fig. 2(d)) further indicates a cladding structure. HRTEM image of square A is shown in Fig. 2(e), and both 0.31 and 0.28 nm of lattice fringe space correspond to (\(\overline{1}11\)) and (111) plane of TaON, respectively, and inset is its FFT pattern which can be indexed to TaON. Fig. 2(f) shows HRTEM image of square B, and the lattice fringe space of 0.36 nm corresponds to (041) plane of TaO\(_2\), and the FFT pattern further confirms that the center part is TaO\(_2\). So the NB is a TaON-cladding TaO\(_2\) NB, namely, TaO\(_2\)@TaON NB. It is attributed to the conversion of TaO\(_2\) NBs from surface to center, however, TaO\(_2\) NBs cannot be all converted under the condition, so TaO\(_2\)@TaON NBs are formed.

A FET based on a single TaON NB is depicted in Fig. 3(a). AFM image of the FET is represented in Fig. 3(b), and the height profile of the corresponding NB is shown in inset. The nanobelt between two electrodes is 1.42 μm in width, 4.34 μm in length, and 92 nm in thickness. Fig. 3(c) displays I-V characteristics at gate voltage (\(V_g\))...
Fig. 1  (a) XRD pattern, (b) low-magnification SEM image (inset: light photograph), and (c) high-magnification SEM image of TaON nanobelts; (d) TEM image of a single TaON nanobelt with inset in the middle showing corresponding HRTEM image, and inset on the upper right corner showing FFT pattern of HRTEM image

Fig. 2  (a) XRD pattern (a peak with star representing Ta2O5, and the rest peaks representing TaON), (b) low-magnification SEM image (inset: light photograph), and (c) TEM image of Ta2O5@TaON composite nanobelts; (d) TEM image of a single Ta2O5@TaON nanobelt; (e, f) HRTEM images of square A and B in (d), respectively with insets showing FFT patterns of corresponding HRTEM images

from –20 V to 20 V. It shows that the conductance of the NB increases monotonically as gate voltage increases, indicating that TaON NB is an n-type semiconductor. The transfer characteristic of the FET at bias of 1 V is shown in Fig. 3(d). The \( I_{ds}-V_{gs} \) plot shows a threshold voltage \( (V_{th}) \) of about 16 V, and a linear-region transconductance \( g_m \) \((dI_{ds}/dV_g)\) of \(3.59 \times 10^{-12} \) A/V. An on-off ratio of 3.4 is measured. The electronic mobility \((\mu)\) can be calculated from the following equations: \(\mu = g_mL/(C_0V_{ds}W)\), where \(W\) and \(L\) are width and length of channel, respectively, and \(C_0\) is the gate capacitance. Assuming a parallel plate capacitor model, \(C_0 = \epsilon_0\epsilon_r/h\).
where $\varepsilon$ is the dielectric constant ($\varepsilon_r=3.9$ for SiO$_2$, $\varepsilon_0=8.854\times10^{-12}$ F/m), and $h$ is the thickness (300 nm) of the gate oxide layer$^{28}$. From above equation, the mobility is calculated to be $9.53\times10^{-4}$ cm$^2$/(V·s).

Fig. 4(a) shows a TaON NB FET which the channel is 0.71 μm in width and 8.5 μm in length, respectively. Fig. 4(b) is the $I$-$V$ curves of the TaON NB FET exposed to different wavelength light and under dark conditions, which exhibits good photoresponse from 254 nm to 850 nm. Based on the data, responsivities to 254, 365, 405, 532, 650, 780 and 850 nm at a bias of 5 V are 199, 237, 347, 53, 45, 28, and 47 mA/W, respectively. The responsivity ($R_\lambda$) and external quantum efficiency (EQE) are related to the number of electron-hole pairs excited by one absorbed photon, so high $R_\lambda$ and EQE correspond to the high sensitivity. $R_\lambda = \Delta I /(PS)$, and $EQE = h\nu R_\lambda/(e\lambda)$, where $\Delta I$ is the difference between the illumination current and the dark current, $P$ is the light power intensity, $S$ is the irradiated area, and $\lambda$ is the light wavelength$^{24}$. Fig. 4(c) shows the responsivities of the FET from 350 nm to 900 nm, so the cut-off wavelength is about 900 nm. As wavelength increases, the change trend is similar to UV-Vis absorption spectrum of the NBs (inset). Here the responsivity at 350 nm approaches that at 400 nm, which may be attributed to the fact that photogenerating electrons of Ta$_2$O$_5$ join in photocurrents because Ta$_2$O$_5$ has only strong absorption at UV region. Fig. 4(d) shows the $I$-$V$ curves of the FET exposed to different-wavelength light. It also shows good photosensitive properties from 254 nm to 850 nm. Fig. 4(e) shows the $I$-$t$ curve of the FET under illumination of 405 nm light (42 mW/cm$^2$) at a bias of 5 V with a photoswitch period of 50 s. Here $R_{405\text{nm}}$, EQE, and PCR are 3.9 mA/W, 1.1×$10^4\%$, and 2, respectively, and rise and decay time of the photoswitch currents is less than 0.2 s, limited by instrument. For comparison, a few
Fig. 4  (a) Photograph of a single TaON nanobelt FET, (b) $I$-$V$ characteristics of the FET illuminated and unilluminated with different wavelength light, (c) responsivities of the FET to different wavelengths with inset showing UV-Vis absorption spectrum of TaON NBs,  
(d, f) transient photoresponses of the FET illuminated by 405 nm (42 mW/cm$^2$) light pulse chopped with a photoswitch period of 1 and 50 s at bias of 5 V and (e) local magnification of (d) from 3.2 s to 5.6 s 

results are included in Table 1. Based on Table 1, single TaON NB photodetector has higher responsivity than single-layer MoS$_2$ and single GaS-nanobelt. Compared with Ta$_3$N$_5$-NB photodetector, the TaON NB photodetector has lower responsivity, but higher PCR, so it is still good photodetector. Under the same illumination conditions, the single TaON NB photodetector higher PCR and responsivity than the single Ta$_2$O$_5$@ TaON NB photodetector, so the former is superior to the latter. It may be attributed that Ta$_2$O$_5$@TaON NB contains less TaON than TaON NB, and bandgap of Ta$_2$O$_5$ (3.9 eV) is greater than that of TaON (2.2 eV), so that photogenerating electrons of the composite NB reduce under illumination of the same light, so the photoresponse dwindles.

3 Conclusion

In the work, a Ta$_2$O$_5$NB template-synthesis route to TaON NB has been provided, which confirms that template-conversion is an efficient way to prepare nanowires (or NBs). Ta$_2$O$_5$@TaON composite NBs can be also prepared by controlling conditions. The phototransistors based on both individual nanobelts show good responses from 254 nm to 850 nm. Compared with Ta$_2$O$_5$@TaON NB, TaON NB shows higher responsivity and PCR, but both may still become good candidates for optoelectronic devices, and can even be used in photocatalysis field.
Fig. 5 (a) Photography of FET based on a single Ta2O5@TaON nanobelt, (b) photoresponsivities of the FET to different wavelengths with inset showing UV-Vis absorption spectrum of Ta2O5@TaON NBs, (c) I-V characteristics of the FET unilluminated illuminated with different wavelength light, and (d) transient responses of the FET illuminated with a 405 nm (42 mW/cm²) light pulse chopped with a photoswitch period of 50 s at a bias voltage of 5 V.

Table 1: Comparison of TaON NB photodetector with others reported

| Photodetector       | Wavelength/Power | Bias voltage/V | $R_s/(\text{A} \cdot \text{W}^{-1})$ | Photoswitch current ratio | Rise time/Decay time Ref. |
|---------------------|------------------|----------------|------------------------------------|---------------------------|--------------------------|
| CdTe NB             | 400 nm/637 μW·cm⁻² | 10             | 12                                 | 1.1                       | ~1.1 s/~3.3 s [27]       |
| Single-layer MoS₂   | 550 nm/80 μW      | 1              | 4.2×10⁻⁴                           | <0.05 s                   | [28]                     |
| GaN NB              | 490 nm/0.5 mW·cm⁻² | 2              | 2.3×10⁻³                           | <0.03 s                   | [29]                     |
| ZrS₃ NB             | 405 nm/10.5 mW·cm⁻² | 5              | 3.9                                | 13                        | <0.4 s [6]               |
| Ta₃N₅ NB            | 450 nm/2.8 mW·cm⁻² | 2              | 99.6                               | ~1.5                      | ~45 ms/40 ms [24]        |
| TaON NB             | 405 nm/42 mW·cm⁻² | 5              | 0.249                              | 11                        | <0.2 s This work         |
| Ta₂O₅@TaON NB       | 405 nm/42 mW·cm⁻² | 5              | 3.9×10⁻³                           | 2                         | <0.2 s This work         |

References:

[1] GLUSCHKE J G, SEIDL J, BURKE A M, et al. Achieving short high-quality gate-all-around structures for horizontal nanowire field-effect transistors. Nanotechnology, 2019, 30(6): 064001–1–7.
[2] LIANG J R, ZHAO Y R, ZHU K L, et al. Synthesis and room temperature NO₂ gas sensitivity of vanadium dioxide nanowire structures by chemical vapor deposition. The Solid Films, 2019, 669: 537–543.
[3] ZHANG Y L, WU X C, TAO Y R, et al. Fabrication and field-emission performance of zirconium disulfide nanobelt arrays. Chemical Communications, 2008(23): 2683–2685.
[4] WU X C, HONG J M, TAO Y R, et al. Controlled growth and field-emission properties of NbSe₂ micro/nanostructured films. Journal of Nanoscience and Nanotechnology, 2010, 10(10): 6465–6472.
[5] TAO Y R, WU X C, XIONG W W. Flexible visible-light photodetectors with broad photoresponse based on ZrS₃ nanobelts. Nanoscale, 2015, 7(34): 14292–14298.
[6] TIAN W, ZHANG C, ZHAI T Y, et al. Flexible ultraviolet-visible light responses of phototransistors based on single and a few ZrS₃ nanobelts. Nanoscale, 2015, 7(34): 14292–14298.
[7] VETTORI M, PIAZZA V, CATTONI A, et al. Growth optimization and characterization of regular arrays of GaAs/AlGaAs core/shell nanowires for tandem solar cells on silicon. Nanotechnology, 2015, 26(19): 3088–3093.
基于单根 TaON 纳米带的光晶体管与紫外到近红外响应

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摘 要：用 Ta2O5 纳米带模板转化法控制合成 TaON 纳米带，典型的纳米带长约 0.5 cm，横截面积 40 nm×200 nm～400 nm×5600 nm。在 SiO2/Si 基片上加工出 TaON 单根纳米带的场效应晶体管；该晶体管的电子迁移率和开关比分别为 9.53×10^{-4} cm²/V·s 和 3.4，在 254~850 nm 范围内显示良好的光响应。在 405 nm（42 mW/cm²）的光照下，外加 5.0 V 的偏压时，光响应为 249 mA/W，开关比为 11。因此，该器件具有良好的光探测性，TaON 纳米带可作为光电子器件的候选材料。另外，实验还控制合成出 Ta2O5@TaON 纳米带，并加工成单根纳米带的场效应晶体管，虽然相同光照条件下的光响应弱于 TaON 纳米带，但仍算是一种好的光电材料。

关 键 词：TaON 纳米带；模板合成；场效应晶体管；光探测器

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