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Metal-semiconductor-metal TiO₂ ultraviolet detectors with Ni electrodes

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In this letter, metal-semiconductor-metal (MSM) TiO₂ ultraviolet (UV) detectors with Ni electrodes have been fabricated. TiO₂ thin films were prepared by sol-gel method. At 5 V bias, the dark current of the detector with Ni electrode was 1.83 nA. High photoresponse of 889.6 A/W was found under irradiation of 260 nm UV light, which was much higher than those of other wide bandgap UV detectors with MSM structure. The high photoresponse was due to the great internal gain caused by the hole trapping at interface. The rise time of the device was 13.34 ms and the fall time was 11.43 s. © 2009 American Institute of Physics. [DOI: 10.1063/1.3103288]

In recent years, UV detectors have drawn much attention because of civil and military applications in engine control, solar UV monitoring, UV astronomy, flame sensors, secure space-to-space communication, biology, and chemistry.¹⁻⁴ In the past, a lot of semiconductor UV detectors based on doped GaN, ZnO, SiC, or diamond were prepared due to their wide bandgap.⁵⁻⁹ However the disadvantages of the UV detectors with these materials are obvious, such as high cost, difficulty of integrating with Si substrate, and complicated fabrication processes. TiO₂ is a kind of wide bandgap (anatase 3.2 eV, rutile 3.0 eV) semiconductor and has been studied in many fields, such as photocatalysis, solar cells, and gas sensors because of its outstanding physical, chemical, and optical properties.¹⁰⁻¹³ In this letter, metal-semiconductor-metal (MSM) TiO₂ UV detectors with Ni electrodes were fabricated on Si substrates, and their photoelectric characteristics were studied.

After a standard rinsing process, SiO₂ was formed on the surface of Si(110) substrate by thermal oxidation method as an insulating layer. Then TiO₂ film was prepared by sol-gel method. The procedure included dissolution of 10 ml tetrabutyl titanate [Ti(OC₄H₉)₄] in 100 ml ethanol (C₂H₅OH), followed by adding 10 ml CH₃COOH, then 10 ml acetylacetone, and 10 ml de-ionized water last. The mixture was stirred at room temperature for 30 min after each reagent was added. The solution was subsequently smeared on the Si(110) substrate by spin coating at the rate of 3000 rpm for 20 s to make sure that the film was uniform. After that, the sample was annealed for 2 h at 650 °C to form polycrystalline oxide film. Then we repeated the spin coating and annealing process four more times.¹³ In order to investigate the optoelectronic characterizations of the film, a Shimadzu UV-1700 Pharma Spec UV spectrophotometer was used to measure the UV-visible absorption spectrum of the film and a VG ESCALAB MKII x-ray photoelectron spectrograph (XPS) was applied to analyze the contents of Ti and O at the surface of the film.

Interdigitated Ni/TiO₂/Ni circular structure was designed and fabricated. The Ni film was deposited by radio frequency magnetron sputtering on top of the TiO₂ film first.

The thickness of Ni measured by a XP-2 profilometer was 160 nm. Then the planar interdigitated electrodes were prepared by standard photolithography and lift-off technique. Both of the finger width and the spacing were equal to 20 μm, and the total active area was 0.38 mm².¹⁴ The picture of the final TiO₂ photodetector device is shown in Fig. 1.

The dark current and the *I-V* characteristics of the device under irradiation of 250 nm UV light were measured by a Keithley 2601 Source Meter. A 30 W deuterium lamp and a monochromator were used to provide monochromatic light. The responsivity of the device was measured by a UV power meter together with a Keithley 2601 Source Meter. An oscilloscope and a 10 mW laser of 266 nm were used to measure the response time of the devices.

The UV-visible absorption spectrum of the TiO₂ film, shown in Fig. 2, indicates that the absorption edge of TiO₂ prepared by sol-gel method is around 320 nm. Compared with the bulk anatase TiO₂ (388 nm), an obvious migration of the absorption peak is observed, which indicates an increase in the band gap of the nanocrystalline TiO₂ due to the size quantization of nanoparticles. The correlation between the particle size and Δ*E_g* which represents the difference between the band gap energy of the bulk anatase and that of the nanocrystalline TiO₂ is given by Brus

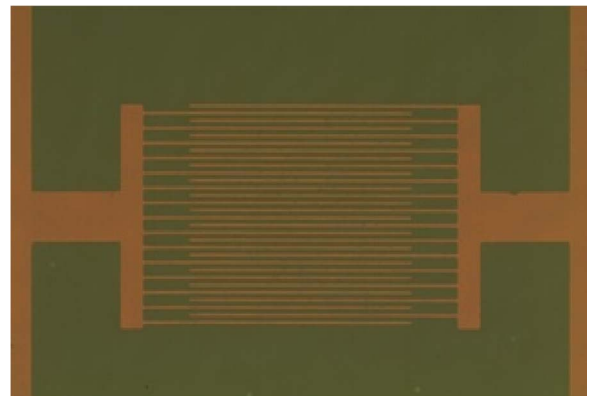
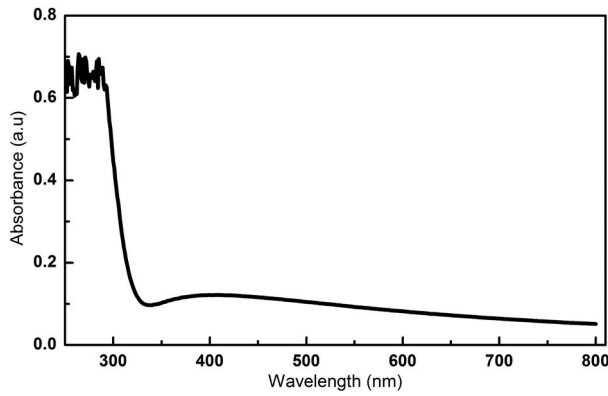


FIG. 1. (Color online) The picture of the final TiO₂ sol-gel photodetector device.

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FIG. 2. The UV-visible absorption spectrum of the TiO₂ film.

$$\Delta E_g = \frac{\pi^2 \hbar^2}{2R^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - \frac{1.82e^2}{\epsilon_R} + \text{polarization terms}, \quad (1)$$

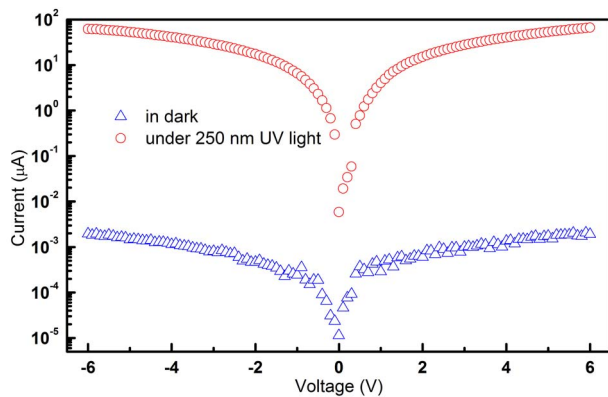
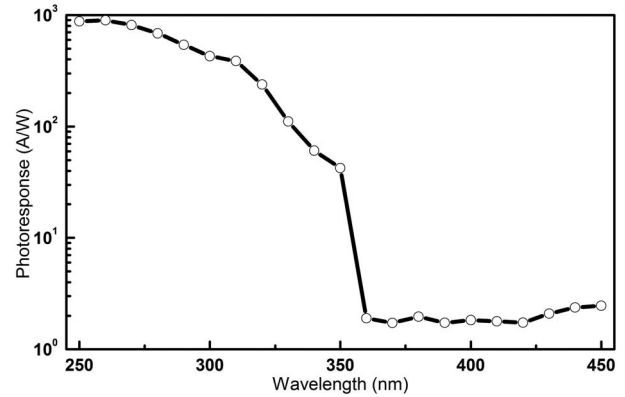
where R is a radius of semiconductor particle, m_e^* and m_h^* are effective masses of the electron and hole in the semiconductor, and \hbar is Planck constant.¹⁵ According to formula (1), the absorption edge will move to the short wavelength as the particle size of TiO₂ decreases. Easwaramoorthi and Natarajan¹⁵ reported that when the size of TiO₂ prepared by sol-gel was 2.6 nm, the absorption edge was about 310 nm, which was consistent with the result of our experiment. The experimental result shows the film we prepared is suitable for the UV detectors.

The I - V characteristics of the Ni/TiO₂/Ni UV detectors are shown in Fig. 3. From the experimental results we can see that the dark current is only 1.83 nA at 5 V bias. Under the irradiation of 15 $\mu\text{W}/\text{cm}^2$ at the wavelength of 250 nm, the photocurrent could reach to 52.91 μA . The ratio of photocurrent-to-dark current is about four orders of magnitude.

Figure 4 shows the spectral response of the Ni/TiO₂/Ni UV detectors under 5 V bias. The responsivity is calculated by

$$R = I/AE, \quad (2)$$

where R is the responsivity, I is the photo current, A is the active area of the device, and E is the irradiance of the UV light which is measured by a standard UV power meter (FZ-A Radiometer, Photoelectric Instrument Factory of

FIG. 3. (Color online) The I - V characteristics of the Ni/TiO₂/Ni photodetector with no irradiation and under the incident light of 250 nm.FIG. 4. The spectral response of the Ni/TiO₂/Ni photodetector.

Beijing Normal University). Under irradiation of 260 nm UV light, the peak photoresponse is 889.6 A/W, which is much higher than those of other wide bandgap semiconductor UV detectors with MSM structure.¹⁶

The high responsivity could be attributed to the great internal gain.¹⁷ The responsivity can also be expressed as

$$R = q\lambda \eta g/hc, \quad (3)$$

where λ is the wavelength of incident light, h is the Planck's constant, c is the light velocity, q is the electron charge, η is the quantum efficiency, and g is the photoelectric current gain. The internal gain g is given by¹⁸

$$g = \tau/\tau_{tr} = \tau\mu_n V/L, \quad (4)$$

where τ is the mean lifetime of the holes, L is the interelectrode spacing, V is the applied bias, and μ_n is the electron mobility of TiO₂. Since V , L , and μ_n are constant in our experiment, the lifetime of the holes (τ) plays an important role in obtaining large gain. It has been reported that there is a large number of oxygen vacancies at the surface of TiO₂ film.¹⁹ In our experiment, the XPS analysis also indicates that the ratio between Ti and O in the surface of the film is Ti:O=1:1.24, which means the existence of oxygen vacancies. These oxygen vacancies can act as hole traps and play a key role in capturing the photogenerated holes. Under a certain operating voltage, the photogenerated electrons would be collected easily by the passive electrodes. Owing to being captured at the interface, the photogenerated holes are difficult to recombine with the electrons. Therefore, the lifetime of holes (τ) would be longer and hence the higher responsivity to be obtained.

The time response characteristic of the devices is shown in Fig. 5. The response time of the device was obtained by measuring the voltage variation in a 5.1 M Ω load resistance in the test circuit. The rise time is 13.34 ms and the fall time is 11.43 s. Compared with the devices with other metal electrodes, there is an obvious improvement in the time response performance. However, from the result we can see that the fall time is still long. As mentioned above, there is a lot of hole traps at the interface. The photogenerated holes are easy to be captured by these traps. Therefore, the recombination between the positive and the negative carriers would reduce and the fall time which is related to the recombination rate would increase correspondingly.

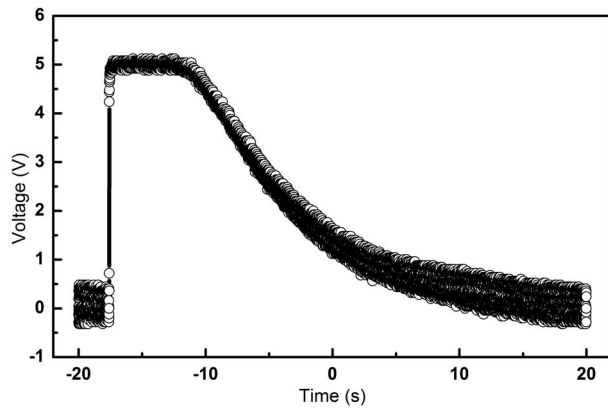


FIG. 5. The time response of the device.

In summary, MSM UV detector with Ni electrode based on TiO₂ thin film was investigated. The absorption edge of TiO₂ prepared by sol-gel method is around 320 nm. The dark current of the detector is 1.83 nA, and high photoresponse of 889.6 A/W is found under the irradiation of 260 nm UV light. The ratio of photocurrent-to-dark current is about four orders of magnitude. The rise time and the fall time are 13.34 ms and 11.43 s, respectively. The high photoresponse is attributed to the large gain caused mainly by the hole traps at the interface.

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