Ultraviolet Photoresponse of TiO₂ Nanotube Arrays Fabricated by Atomic Layer Deposition

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We used atomic layer deposition with anodic aluminum oxide, to fabricate self-aligned TiO₂ nanotube arrays, on a Si substrate, at 400°C. Numerous p-n nanojunctions can be fabricated using this approach. In the absence of the external application of a bias voltage, these crystalline nanotubes make very sensitive ultraviolet sensors. The sensitivity is a result of the built-in voltage, generated by the nanojunction formed between the TiO₂ nanotubes and the Si substrate, which separates electron-hole pairs and produces photocurrents. In addition, the one-dimensional structure of the TiO₂ nanotubes provides a well-defined path for the transportation of the photo-generated carriers.

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One-dimensional (1D) semiconductor nanostructures have attracted considerable interest in recent years, because of their unique physical and chemical properties. TiO₂ has a wide bandgap of 3.2 eV (anatase) and it is an n-type semiconductor. In addition, because nanotube structures have a large surface-to-volume ratio, TiO₂ nanotubes have been extensively studied and applied to photocatalysis and dye-sensitized solar cells.

Since modern manufacturing processes mostly use Si as a substrate, it is important to consider whether a manufacturing process can incorporate a Si substrate. Current studies of TiO₂ nanotube arrays are mostly carried out using the anodization of a Ti foil. Although this method allows the fabrication of very neatly arranged TiO₂ arrays, the method cannot incorporate a Si substrate.

Atomic layer deposition (ALD) is a deposition technique in which the film thickness can be precisely controlled and which provides excellent step coverage, because its coating method is controlled by surface reaction. Anodic aluminum oxide (AAO) is a highly regular template material and has a manufacturing process that can easily incorporate various substrates. If these two techniques are combined, regularly arrayed, thin-walled TiO₂ nanotube arrays can be grown on a p-type Si substrate. This method has been published elsewhere.

TiO₂ nanotube arrays, deposited on a p-type Si substrate, form p-n nanojunctions. These nanojunctions may increase the photoresponse properties of TiO₂, but only a few studies have reported the photoresponse properties of TiO₂ nanotube arrays on a Si substrate. In addition, during photoresponse measurement, a bias of a few volts is applied to the nanostructures. Photoresponse measurement without bias has not been reported.

In this study, we used AAO and ALD to fabricate TiO₂ nanotube arrays, at 300 cycles, on a p-type Si substrate. Using transmission electron microscopy (TEM), we examined TiO₂ nanotube arrays. We examined the TiO₂ nanotube arrays, using an ultraviolet (UV) sensor, and found that TiO₂ nanotube arrays were very sensitive to UV light, without the need for a bias voltage.

Experimental

The fabrication procedures for the AAO and ALD have been reported in our previous publication. To investigate the photoresponse of these nanotubes, E-gun deposition was used to deposit a 200-nm layer of indium tin oxide (ITO) on the upper surface of the TiO₂ nanotubes. This acted as an upper electrode, while the Si substrate acted as the lower electrode. The Si substrate is p-type and doped by boron at 1.5 × 10¹⁶ atom/cm³. The resistivity of the Si substrate is about 1–5 Ω cm. The wavelength of the ultraviolet (UV) source was set at 365 nm and its power was 21 mW/cm². The sample area was 9 mm². A Keithley-2400 was used to measure the photocurrent.

Results and Discussion

Regular arrays of n-type TiO₂ nanotubes can be fabricated on a p-type Si substrate, using this approach. Figure 1a shows the plan-view TEM images, for TiO₂ nanotubes on the AAO template. The average wall thickness of the nanotubes is measured to be 17.3 nm and the thickness appears to be very uniform. Figure 1b presents the cross-sectional TEM image, for the nanotubes in the AAO nanotube arrays. The thickness is also quite uniform along the direction of the AAO nanotubes. A selective area diffraction pattern of the TEM shows the TiO₂ nanotubes to be crystalline anatase.

Approximately 19.0 nm of TiO₂ was deposited on the bottom of the AAO nanotubes on the Si substrate, during the ALD process. The differing thickness of the TiO₂ is due to the different mechanisms for TiO₂ growth, on Si and AAO. A layer of native oxide, approximately 2 mm thick, is present between the TiO₂ nanotubes and the Si surface. The TEM image for the interface was reported in our previous study. The native oxide is not as dense as thermal oxide, therefore, we speculate that TiO₂ still has some contact with the Si to form hetero-junctions. In addition, our experimental results show that we can still obtain photocurrents, indicating that the native oxide is not thick enough to prevent the formation of the hetero-junctions. The shape of each individual p-n nanojunction approximately a circle or an oval. It is estimated that p-n nanojunctions cover 79% of the Si surface. This percentage was calculated using the plan-view SEM image in Fig. 1c, and the equation: \[ \frac{\pi r^2}{N} \times \% \], where r is radius of nanotube and N is the number of nanotubes. Near the bottom of the AAO nanotubes, the TiO₂ film forms p-n nanojunctions with the Si substrate, as indicated by the arrows in Fig. 1b. These nanojunctions may be to the explanation for the performance of the TiO₂ nanotubes, with respect to UV photoresponse.

TiO₂ nanotubes, produced by ALD, can perform as a UV light sensor. When we analyzed the I-V characteristics of the TiO₂ nanotubes on Si substrates, we found that changes in electrical current occurred when the nanotubes were exposed to UV light. The experimental setup for the measurement of photoresponse is shown schematically in Fig. 2a. For this study, ITO was deposited on the top surface of TiO₂ nanotubes as an upper electrode, and the bottom electrode was Si substrate.

Figure 2b shows the I-V curve for the device (ITO/TiO₂ nanotubes/Si), with no UV illumination, and a change in bias voltage, from −20 V to 20 V. It can be seen that the curve for current is asymmetrical: the current is almost zero, when the bias voltage is negative, whereas when the bias voltage is positive, the current increases significantly, with increasing bias voltage. There is a 0.2 mA increase in current, when the bias voltage is 20 V. The asymmetrical nature of the I-V curve indicates that the nanojunction
formed between the TiO$_2$ nanotubes and the Si substrate exhibits rectifying behavior, suggesting the existence of an inherent voltage at the junction of TiO$_2$ nanotubes and the Si substrate. It is worth noting that the forward bias is about 10 V, as shown in Fig. 2b, which is a very high value for a p-n junction. This may be attributable to the high-resistivity TiO$_2$ nanotubes. Some of the voltages may drop across the TiO$_2$ nanotubes. Thus, the real forward voltage in the p-n junction should be smaller than 10 V.

The ITO/TiO$_2$ nanotubes/Si device, fabricated for this study, has a sensitive photoresponse to UV light. Figure 2c shows the curve for current change for the device, when the UV light is on and off. The UV light remained on, or off, for 15 seconds and the current was measured once every second. No external voltage bias was applied. From Fig. 2c, it can be seen that the dark current for the device is zero, when there is no UV light. When UV light is switched on, the device rapidly generates a 0.35 $\mu$A photocurrent and reaches saturation, within one second. When the UV light is turned off, the photocurrent of the device rapidly decreases to zero, within a second.

For this study, we repeated the measurements for 5 cycles. The results of the measurements indicated that the ITO/TiO$_2$ nanotubes/Si device was a very sensitive and stable detector for UV light. The sensitivity is calculated using $\frac{I_{ph}}{P_0}$, where $I_{ph}$ is net photocurrent and $P_0$ is energy of the incident UV light. The sensitivity of the device was measured to be $1.9 \times 10^{-4}$ (A/W). The typical sensitivity value for a commercial UV sensor is 0.1 $\sim$ 0.2 (A/W). The low sensitivity recorded in this study is attributable to a lower photocurrent, due to the absence of external bias.

It must be emphasized that, for this study, no external bias voltage was used, when UV light detection was measured. In previous studies related to UV light detection, external bias voltage was applied to the sensor material. This voltage bias was applied, because electron-hole pairs need to be separated, after the UV light shines on the sensor material; if there is no external bias voltage to act as a driving force, at this time, the electrons and holes cannot move and the electron and hole will recombine, resulting in no photocurrent. The nanojunction between TiO$_2$ nanotubes and Si, formed in this study, has an inherent voltage that can directly provide the driving force required for the movement of electrons and holes, generated by the UV light.
The energy band diagram is shown schematically in Fig. 3. There is a depletion region at the interface between Si and TiO$_2$ nanotubes. With reference to the diagram, it is possible that, when UV light shines on TiO$_2$ nanotubes, electron-hole pairs are generated in the nanotubes. Since the inherent voltage at the TiO$_2$-Si junction causes the electrons to move towards the TiO$_2$ and the holes to migrate towards the Si substrate, a photocurrent forms. It is worth noting that ITO was used as the upper electrode and hetero-junctions of ITO/TiO$_2$ could form there, as shown in Fig. 3. These hetero-junctions may also affect the photocurrent.

Chang et al. reported that the ITO/TiO$_2$ hetero-junction may produce a photocurrent opposite to that generated at the TiO$_2$/Si nano-junction. However, this photocurrent drifts from the right-hand side to the left-hand side, as shown in Fig. 3. Therefore, the TiO$_2$/Si nanojunction may have a dominant effect on the photocurrent and the effect of ITO/TiO$_2$ hetero-junctions on photocurrent may be ignored, for the purposes of this study.

The ITO/TiO$_2$ nanotubes/Si device’s 1-D structure may explain its sensitive and stable performance, in the detection of UV light. A 1-D structure provides a specific path for photo carriers during transport, and this specific path allows for the efficient transport of photo carriers, so 1-D TiO$_2$ nanotubes should perform better than 2-D TiO$_2$ thin films with respect to photoresponse.

**Conclusion**

By integrating ALD and AAO technologies, self-aligned TiO$_2$ nanotube arrays were generated on a Si substrate. The 1-D arrays of TiO$_2$ nanotubes provide a well-defined transportation path for the photo-generated carriers. In addition, the formation of nanojunctions between TiO$_2$ nanotube arrays and the Si substrate produces an inherent voltage, so the device is sensitive to UV light without the need for an external voltage bias. These results indicate that TiO$_2$ nanotube arrays have great potential as UV sensors.

**References**