Synthesis of Anodic TiO$_2$ Nanotube Arrays Annealed at 700$^\circ$C for UV Photodetector

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Abstract. Anodic titanium dioxide (TiO$_2$) nanotube arrays on Ti foil were synthesized using electrochemical anodization technique and annealed at 700 $^\circ$C without annihilating the nanotubular assemblies. The nanotubular structure was used to fabricate UV photodetection device based on Metal-Semiconductor-Metal. The photodetection device exhibited UV-sensitive photoresponse characteristics due to the mixed anatase and rutile phases of the TiO$_2$ nanotube arrays. The photoresponse analysis showed good sensitivity to UV light irradiation with excellent stability and reproducibility. Moreover, the UV photodetector revealed the current gain is 7, response time is 0.77 s and decay time is 0.79 s, respectively at biased voltage 4 V. As mentioned above, the UV photodetector based on mixture of anatase and rutile phase nanotube arrays is a recommended nano-optoelectronic apparatus that is remarkably applicable over Ultraviolet band.

1. Introduction
Anodic TiO$_2$ nanotube arrays (ATNAs) manufactured by electrochemical anodization of Ti foils has been widely inspected over the last decade, on account of the prospective applications in nano-optoelectronic apparatuses [1]. In contrast to a crystalline thin films or arbitrarily oriented nanostructures, ATNAs are supposed to tend toward unidirectional carriers transport inside and along the nanotubes that drive more charge mobility which is vital for devices performances. However, many recent researches have pointed out that the carriers transport speed in nanotubes is not superior to that in nanostructure films because of the exciton-like trap centres presence that undermine the performances of ATNAs-based nano-optoelectronic devices [2].

The trap centres in ATNAs architecture can be reduced by high temperature annealing in oxygen ambience that causes reduction in the oxygen vacancies. Additionally, the ATNAs architecture main significance is the photoactivity, but it can only be retained up to 600 $^\circ$C, beyond this point a conversion from anatase to rutile phase and the destruction of orientation and alignment was observed. Keeping the nanotubular structure at a temperature higher than 600 $^\circ$C with reduced trap centres remains a challenge towards achieving better photoactivity of the TiO$_2$ nanotubes-based nano-optoelectronic devices [3].

In actuality, the vast particular surface area, well-defined paths for carriers transport and exclusive ultraviolet spectrum absorption made ATNTs architecture match the UV spectrum detection [4]. Many studies of TiO$_2$ nanostructures film-based UV photodetector have been reported [5]. But to this date, no reports have been prepared to improve the UV photodetectors built on the TiO$_2$ nanotubes annealed at 700 $^\circ$C. While annealing TiO$_2$ nanotube arrays at 700 $^\circ$C might give us exceptional morphological features which would brand it as an optimal choice for UV photodetection, but the difficulty and trickiness in its manufacturing made it a challenge for its improvement.
In this current study, we have utilized an innovative method by annealing in typical atmosphere to assemble a mixed of anatase and rutile phase TiO$_2$ nanotube arrays on Ti foil to manufacture UV photodetector. The UV photocurrent characteristics were studied systematically. The device showed well-gain, speed-response and remarkable reproducibility and stability in photodetection with period.

2. Experimental Method

Two-step anodization under controllable conditions was applied in a Teflon cell contains Fluoride ions electrolyte for growth of anodic TiO$_2$ nanotube arrays (ATNAs) films. This process was explained in details in our previous study [6]. The annealing process of the amorphous ATNAs film was implemented at 700 °C under a stream of water vapor/nitrogen gas inside a cylinder furnace for 3 h to avoid the failure of nanotubular arrangement and forming bi-phase of anatase and rutile nanotube arrays. The mixed phase of anatase and rutile nanotube arrays was fulfilled to manufacture UV photodetector based on metal-semiconductor-metal. The Ni electrodes with thickness of 150 nm were precipitated by using RF sputtering evaporating at room temperature on a metal facade based on the pattern configuration of the two contacts with four branches in each side. The I-V characteristics and photocurrent response for the manufactured device were determined at various bias voltages (0.5, 2 and 4 V) and under UV irradiation (365 nm, 1.2 mW/cm$^2$) by using voltage source (Keithley model-4200) at Laboratory temperature. ATNAs films were pictured by FE-SEM (Nova NanoSem-450) instrument. Crystalline structural patterns were achieved by High Resolution-XRD (PAnalytical X’pert PRO MRD PW3040) with a Cu K$_\alpha$ source of wavelength (0.154 nm). Diffuse reflectance spectrum was attained via the spectral variety from 200 to 800 nm by using UV-VIS-NIR spectrophotometer (Agilent Cary 5000).

3. Results and Discussion

Figure 1(a) illustrates the FESEM over-view portrayal of as-prepared ATNAs film. Highly-ordered hexagonal with honeycomb-like lattice structure and pore width around 80 nm was witnessed. Figure 1(b) illustrates the FESEM cross-sectional view portrayal of as-prepared ATNAs film, since the tube-like walls seem to be flat and smooth. At high temperature annealing of 700 °C revealed in Figure 1(c), the honeycomb-shape pores became untidy and contracts in dimension due to the growing of the large crystalline particles of rutile phase. Figure 1(d) illustrates the FESEM cross-sectional view portrayal of annealed ATNAs film at 700 °C. It is quite clear that the tube-like morphology of the annealed sample has considerably converted in contrast with the as-prepared sample. When the nanotubes were spotted prudently, the mesoporous configurations on the inflated wall of honeycomb-shape patterned nanotubes can be witnessed and the tube-like structures were well kept at elevated annealing temperature, this is due to the stream of water vapor/ N$_2$ gas inside a tube furnace under ambient atmosphere during the annealing process. It impeded the release of hydroxyl ions from TiO$_2$ nanotube walls and inhibited the reducing number of hydroxyl bonds [7]. Hence, it permitted the large crystalline of the rutile phase on the nanotubes walls to preserve its integrity with anatase crystalline without annihilating nanotubular assemblies.

Figure 2 demonstrates the x-ray diffraction pattern of ATNAs film annealed at 700 °C. A partial conversion from unstable anatase phase into stable rutile phase was observed. The anatase peaks at 25°, 38.5°, 48.2°, 53.8°, 55° and 62.8° were matching with the crystallographic planes patterns (101), (112), (200), (105), (211) and (204). The rutile peaks at 27.3°, 39° and 54° were matching with the crystallographic planes patterns (110), (101), and (211).

The diffuse reflectance performance was completed to determine the energy bandgap of ATNAs film annealed at 700 °C. The diffuse reflectance measurements were attained in the variety of 200–800 nm, as revealed in Figure 3 (a). The Kubelka-Munk function $F(R)$ was applied to compute the direct energy bandgap, as given by Equation (1) [8].

$$F(R) = \frac{(1-R)^2}{2R}$$  (1)
Figure 1. FESEM images (a, b) show the top-view and cross-sectional of as-prepared anodic TiO$_2$ nanotube arrays sample and (c, d) show the top-view and cross-sectional of annealed anodic TiO$_2$ nanotube arrays sample at 700 °C, respectively.

Figure 2. XRD pattern of anodic TiO$_2$ nanotube arrays film annealed at 700 °C.
Figure 3(b) displays \((F(R) \cdot h\nu)^2\) vs. \(h\nu\) diagram. The direct energy band gap (\(E_g\)) can be valued by supposing a straight-line section of the \((F(R) \cdot h\nu)^2\) to pass across the \(h\nu\) axis. The \(h\nu\) value was 3.4 eV for ATNAs film annealed at 700 °C. This value is matching with the previously results [9]. Furthermore, this direct energy bandgap value would permit a high absorption of UV photons to generate an electron–hole pairs.

![Graph](image)

**Figure 3.** (a) Diffuse reflectance spectrum and (b) Tauc plot of the Kubelka–Munk function of anodic TiO₂ nanotube arrays film annealed at 700 °C.

Figure 4(a) illustrates the schematic-sketch of the device for measuring the current–voltage characteristic and photoresponse under dark and UV irradiation. Figure 4(b) illustrates the (I-V) characteristic of the device irradiated by 365 nm and 1.2 mW/cm² is symmetrical correlation and non-linearity performance, which confirmed the Schottky barrier between the Ni contacts and TiO₂ nanotubes [10]. The photocurrent mechanism, mainly generating the excited electron-hole pairs by incident UV photons with wavelength of 365 nm, were sufficient to produce the photo excited carriers (electron-hole pairs) that were collected in the depletion zone between TiO₂ nanotubes and Ni metal, and the applied bias voltage caused in the splitting of electron-hole pairs and free electrons movement to the Ni metal contacts [11].

The photocurrent gain (\(g\)) is an important parameter that used to estimate the photodetector performance, It is expressed by the Equation (2) [12]

\[
g = \frac{I_{\text{light}}}{I_{\text{dark}}} \]  

where, \(I_{\text{light}}\) is the light current, \(I_{\text{dark}}\) is the dark current. The gain value of the photodetector was estimated in Figure 4 (b) to be approximately 7 at the bias voltage of 0.5, 2 and 4 V, respectively. The vital value of gain was recognized to be the greater surface to volume ratio and excellent crystalline quality of the nanotubes. The greater surface to volume ratio of the nanotubes, the greater the collection of the UV light, thus more surge of the photocurrent. The excellent crystalline quality of the nanotubes drops the density of color centers caused by defects, consequently improving the photoresponse considerably [10].

Figure 4(c) illustrates the current-time pulses measured at 0.5, 2, and 4 V bias voltages upon on and off switch by UV irradiation of 365 nm. It was revealed that the extreme value of current was stable during several pulses for the bias-voltages, showing the outstanding reproducibility and stability performance of the photodetector. Furthermore, the upright rise and fall times with minor exponential in the current cycles showed that the instigate of the photocurrent from the band to band electron transition [13]. Furthermore, the photocurrent upsurges with increasing the bias-voltage, which consequently increased the charge drift velocity due to decreasing in charge transit time [14]. The most interesting parameters to evaluate the UV photodetector performance were the response time (\(T_{on}\)) and
recovery time ($T_{\text{off}}$). As shown in Figure 4(c), by escalating the district upon switching on and off of the UV irradiation observed that ($T_{\text{on}}$) were 0.87, 0.78, and 0.64 s, respectively and ($T_{\text{off}}$) were 0.87, 0.92, and 1.09 at bias-voltage 0.5, 2 and 4 V, respectively.

![Figure 4](image)

Figure 4. (a) Schematic-diagram of the UV photodetector. (b) The (I-V) characteristics of the photodetector under dark and light illumination. (c) Photoresponse-characteristics of the photodetector at bias voltages 0.5, 2 and 4 V, respectively.

4. Conclusion
In summary, anodic TiO$_2$ nanotube arrays (ATNTs) on Ti foil annealed at 700 °C was fruitfully manufactured using a novel annealing process method. The special morphological features of the nanotube arrays were exploited to fabricate UV photodetector with high-performance photoresponse, remarkable reproducibility and stability over time. The excellent-performance of the photodetector shows that anodic TiO$_2$ nanotube arrays with mixed of the anatase and rutile crystalline have a favorable future in the nano-optoelectronic applications.

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