A SOLAR CELL BASED ON TiO_2 NANOTUBES COMBINED WITH AN ELECTROCHEMICAL CAPACITOR BASED ON NANOPOROUS AL_2O_3

Sh.O. EMINOV, A.Kh. KARIMOVA, S.H. ABDULLAYEVA, J.A. GULIYEV, E.M. AKBAROV, I.I. GURBANOV, S.A. ALIYEVA
Institute of Physics of the Ministry of Sciences and Education Republik of Azerbaijan, H. Javid pr., 131, AZ1143, Baku
ceferquliyev87@mail.ru

Hybrid systems have gained significant attention among researchers and scientists worldwide due to their ability to integrate solar cells and supercapacitors. Subsequently, this has led to rising demands for green energy, miniaturization and mini-electronic wearable devices. These hybrid devices will lead to sustainable energy becoming viable and fossil-fuel-based sources of energy gradually being replaced. A solar cell system is an electronic device that mainly functions to convert photon energy to electrical energy using a solar power source. This paper describes an integrated system in which a NiO_2 nanotubular supercapacitor serves as an energy storage device, while TiO_2 nanostructures operate as energy conversion devices. The main operations for the fabrication of the proposed device are listed. It was shown that the design features of the device allow combining and simultaneous execution of some similar fabrication operations, which would have to be carried out in the case of separate manufacture of the constituent elements of the device.

Keywords: Solar cell, supercapacitor, Anodic alumina, TiO_2, ITO, nanopores, nanotubes.
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1. INTRODUCTION

Titanium dioxide (TiO_2) is a wide bandgap semiconductor with a bandgap ranging from 3.0 to 3.2 eV. It is capable of converting light energy into chemical redox energy, making it an ideal material for harvesting solar energy and maximizing conversion efficiency in various applications, such as photovoltaics, microwave sensing, and photocatalysis. TiO_2-assisted photoelectrolysis of water is achieved using a closed-circuit photoelectrochemical solar cell comprising a TiO_2 anode and a Pt counter electrode exposed to near-UV light. Typically, the anatase phase of TiO_2 exhibits the highest efficiency for solar cell performance. Similarly, nanoporous anodic alumina (NPAAO) is an electrically insulating, optically transparent, and chemically stable material widely used in electronic, optoelectronic, and sensing devices. It also serves as a template for the synthesis of metallic and semiconductor nanowires. Both NPAAO and free-standing vertically oriented nanotube TiO_2 (TNT) can be fabricated via anodization and heat treatment of thin Al and Ti layers deposited on different substrates, such as Si or conductive glass substrates (In_2O_3:Sn or ITO-covered), using electron beam evaporation or magnetron deposition. The electrochemical anodic oxidation process can be carried out in an electrochemical cell with a two- or three-electrode system. A Ti- or Al thin layer serves as the working electrode (anode), Pt acts as the counter electrode, and a standard voltage source or a high-voltage potentiostat is employed.

Due to the intermittent and variable nature of solar energy intensity, which varies greatly depending on the season and time of day, combining solar cells with energy storage devices, such as Li-ion batteries and supercapacitors (SC), in a single power unit component is essential [1, 2]. In this study, we have utilized both AAO templates and TNT thin layers [2, 3] to propose a device that integrates energy conversion (TNT-based solar cell) and energy storage (SC based on NiO nanotubes synthesized in AAO nanopores) into a single system. The solar cell and capacitor are fabricated on opposite sides of a common glass slide wafer, both of which are covered with a conductive ITO layer. The TNT-based solar cell is positioned on the front side of the device to receive light, while the SC is located on the rear side. Alternatively, a dye-sensitized solar cell or Grätzel cell [4] can be used as the solar cell component in the proposed hybrid device.

The supercapacitor component consists of freestanding NiO_2 nanotubes that are electrochemically grown inside AAO nanopores and embedded in the electrolyte. They are electrically connected to the positive electrode through the ITO layer, while activated carbon serves as the negative electrode. The ITO layer acts as both the rear electrode for the solar cell and the positive electrode for the supercapacitor.

2. EXPERIMENTAL

2.1 Preparation of the Glass/ITO/AAO structure

To implement the solar section of the subject device, as the first preparation stage, glass substrates were ultrasonically degreased in acetone and isopropyl alcohol, rinsed in deionized water, and subsequently dried in poor nitrogen flow for 15 minutes before loading into the deposition chamber. Afterward, substrates were loaded into the vacuum deposition chamber of the Leybold Heraeus-Z550 RF magnetron sputtering system equipped with a turbomolecular vacuum pump system. Initially, ITO films with different film thicknesses from 200 to 300 nm were prepared on an unheated glass substrate by radio-

131, H.Javid ave, AZ-1143, Baku
Institute of Physics
E-mail: jophphysics@gmail.com

frequency (RF) magnetron sputtering using a 75 mm diameter ITO target (90% In_2O_3 and 10% SnO_2). The target-to-substrate distance was fixed at 10 cm. The sputtering chamber was vacuumed to a base pressure of 5 10^{-3} Pa and a pure argon gas flow of 5 sccm was introduced as a reactive sputtering gas through a mass flow controller. Before deposition, the target was RF pre-sputtered in argon plasma for 20 minutes at a power level of 50 watts to remove contaminants from the surface of the target. The ITO deposition process was conducted at a working pressure of 3.3 Pa and with the power level fixed at 200 W for different deposition times (20-40 minutes), depending on the thickness of the film. Thereafter, an Al film with a thickness in the range of 200 to 300 nm was deposited onto a glass/ITO substrate using a 75 mm diameter aluminum target (99.99% pure) under similar conditions. Following that, the electrochemical anodization of the Al film was performed in a two-electrode cell using 0.4 M oxalic acid solution at constant potentials from 10 to 40 V at a temperature of 3°C to 5°C for 10 to 20 minutes.

The digital photographs in Figure 1 depict the aluminum deposited on the glass/ITO substrate using the magnetron sputtering method, both before and after the oxidation process. The photographs are arranged to show the top and bottom sides correspondingly.

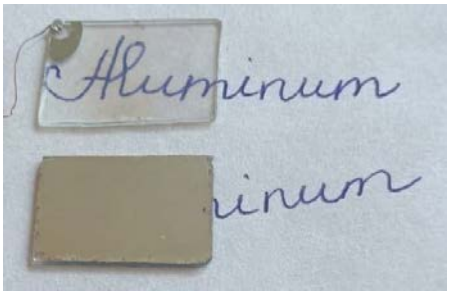

Fig. 1. Digital photographs of AAO (top) and aluminum on glass/ITO substrate (bottom)

2.2 Preparation of the glass/ITO/TiO_2 structure

Since the procedure for obtaining the ITO layer on glass in the glass/ITO/TiO_2 nanostructure by magnetron sputtering is the same as the procedure for obtaining the ITO layer in the glass/ITO/AAO structure, this method of obtaining the ITO layer has been explained in detail above. After this processes, the titanium thin film with a thickness in the range of 150 to 200 nm was RF sputtered on the previously obtained ITO layer in the same chamber using a titanium target (99.5% purity) with a 75 mm diameter at a power level of 150 W under conditions similar to the ITO deposition process. Then, TiO_2 thin film was formed by electrochemical anodization of as sputtered Ti film in a homemade two electrode cell using a Pt mesh as a counter electrode and Ti/ITO/glass substrateas an anode under a constant potential ranging from 10 to 60 V at 3 to 5°C. The mixture of ethylene glycol, 0.4 wt% ammonium fluoride, and 2 vol% distilled water was used asan electrolyte. The duration of anodization ranged from afew minutes to several tens of minutes, depending upon the thickness of the Ti layer. To maintain the set temperature during the anodization process, the electrochemical cell was kept in a container with icy water.The samples were removed from the electrolyte after they became optically transparent, and the value of the anodization current dropped to zero. The anodized samples were washed in isopropyl alcohol and distilled water for about 5 minutes and then blowdried with nitrogen. The obtained glass/ITO/TiO_2 structures were finally annealed for 2 hours in the airat 450°C to improve the crystallinity and electrical characteristics of both the external TiO_2 and the internal ITO thin films.

The digital images of the samples presented in Figure 2 show the change in the appearance of the Ti-coated glass/ITO structure after anodizing as well as after subsequent thermal annealing. During the anodization process, the initially opaque Ti film (a) gradually transforms into TiO_2 and becomes transparent (b). Upon subsequent thermal annealing at 450ºC, the optical transmission and transparency of the samples decrease as compared to non-annealed. This is because, upon annealing in the air, some additional oxygen vacancies are introduced into the film, on which the light is scattered and the light absorption increases.

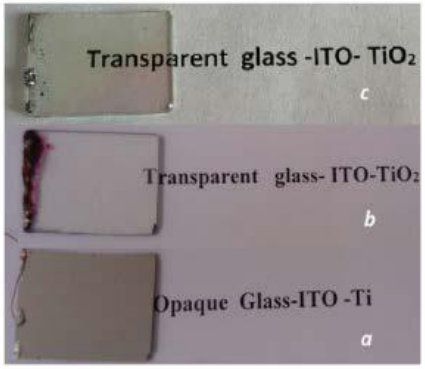

Fig. 2. Optical images of the structure before (a), after oxidation (b), and upon annealing (c)

3. RESULTS AND DISCUSSION

Figure 3 schematically illustrates the cross-section of the proposed power unit. In Figure 3, it can be observed that a transparent glass slide (1) is covered on both sides with a conductive ITO thin film (2), with one side coated with TiO_2 and the other side with an AAO template. The solar cell is positioned on the front side of the glass slide, while the SC component of the device is located on the rear side. The key manufacturing steps for the proposed device are listed below:

• The deposition process involved coating both sides of a glass plate with ITO layers, followed by the deposition of aluminium and titanium layers on each side. Subsequently, anodic oxidation was performed on both sides to synthesize a nanoporous AAO and TiO_2 nanotube structure;

• Ni nanotubes were created through the electrochemical deposition of nickel into AAO nanopores on the capacitor side;
• The entire structure was sintered in air at temperatures ranging from 400 to 500°C to facilitate the formation of NiO2 nanotubes through the oxidation of nickel;
• The next step involved installing a porous separating layer and a porous carbon negative electrode in the supercapacitor. Following that, an array of NiO nanotubes was filled with a suitable alkaline electrolyte and sealed;

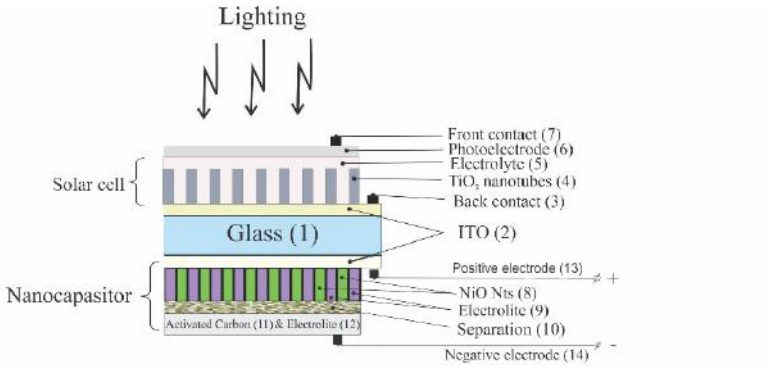

Fig. 3. Cross-section of the integrated power unit

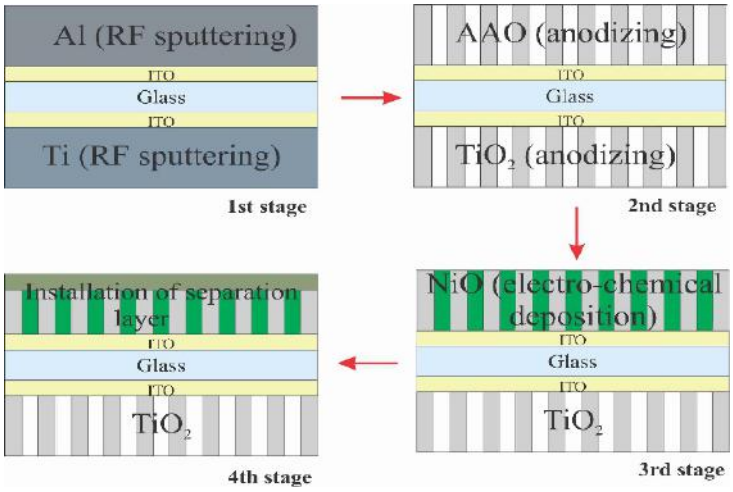

Fig. 4. Flow chart of the 1 to 4 stages of the fabrication process.

The manufacturing steps are described below.
1. The deposition process involved magnetron deposition of ITO, aluminium, and titanium layers. Initially, ITO was deposited on both sides of the glass substrate. Subsequently, aluminium was deposited on one side, while titanium was deposited on the other side.
2. Simultaneous anodic oxidation of the glass/ITO substrate was performed, with one side being aluminium and the other side being titanium, in order to create AAO and TiO_2 templates on the glass/ITO plate.
3. Ni nanotubes were electrochemically deposited within the AAO templates on the rear side.
4. The structure was sintered in air at 400 to 500°C, resulting in the formation of NiO_2 nanotubes through the oxidation of Ni in an air environment.
5. Preparing the supercapacitor side.
A flowchart of the initial 1 to 4 stages of the manufacturing process is shown in Figure 4.

As it can be seen from Figure 4, the manufacturing stages numbers 1, 2, 3 and 4 used for the manufacture of solar cell and supercapacitors, are similar and are carried out simultaneously. Therefore, the design features of the device allow combining and simultaneous execution of some similar fabrication operations that would have to be carried out in the case of separate fabrication and manufacture of the constituent elements of the device, thereby significantly reducing the number of production operations. As opposed to constructing each component independently, we believe that using the same production procedures will reduce the amount of materials and energy needed and lower the cost of solar energy collection. In addition, putting the capacitors on the same substrate as the solar cell will make the system more compact. To date, we have carried out experimental studies on the practical implementation of the solar cell part of the device. At present, our efforts are directed toward the practical implementation of the capacitor part of the device.

4. CONCLUSION

To realize the proposed device structure of AAO(NiO)/ITO/Glass/ITO/TiO_2, we employed RF magnetron sputtering to obtain highly ordered TNT and AAO arrays with a high degree of optical transmission. Subsequent anodic oxidation and thermal annealing were also applied. Additionally, we developed a technique for the electrochemical deposition of nickel nanotubes into AAO templates and doping of TNTs with various impurities, which enhanced their photosensitivity from the UV region to the visible spectra. The device design enabled the combining and simultaneous execution of similar fabrication operations. The films were characterized using scanning electron microscopy, XRD, Raman spectroscopy, UV-vis spectrometry, and spectroscopic ellipsometry. The resulting structure, with an outer TiO_2 layer having an extended nanotube surface and an electrically conductive ITO layer, exhibited strong absorption of solar radiation, making it well-suited for solar energy harvesting applications. Thus, the proposed device is a fully integrated device with a monolithic structure, where the solar cell and energy storage segments share a common substrate in the form of a transparent and conductive glass wafer. This device can be referred to as a photo-supercapacitor or solar capacitor.

Due to its more compact structure, fewer wiring requirements, and shared substrate and electrodes, the proposed device may have higher volumetric and gravimetric energy densities compared to a solar power system composed of separate components. In addition, the fabrication of this device involves the integration of multiple solar cells and SC fabrication technologies, allowing for the combining and simultaneous execution of some similar fabrication operations. This reduces the overall number of operations required compared to the separate manufacture of the constituent elements of the device. The integration of solar cells and supercapacitors into a single hybrid device, in which energy-harvesting and storing units are combined into one system, is expected to meet the rising demand for green energy and the miniaturization of wearable devices.

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