Construction of Nanobiomaterials using Chemical Method

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Abstract: ZnO "nanorods" perpendicularly aligned grown on (FTO) coated quartz substrates by using a hydrothermal method. Energy Dispersion X-Ray Spectrometry (EDXS) showed the elements of "Zn" and "O", moreover prove the high purity of ZnO nonmaterial. The element ratio of "Zn" and to "O" is quantitatively managed equal (89.4:10.6).

TiO2 "nanotubes" grown on "Ti" foil by using hydrothermal and anodization method. The major components of the TiO2 "nanotube" titanium and oxygen with compound percentage for the "Ti" and "O" are (65.1:34.9) respectively.

Keywords: ZnO, FESEM, XRD, TiO2, nanotubes, Anodic oxidation.

Introduction:

Transparent conducting oxides (TCO) are important to development the photonic devices that take a great interest in the few years ago [1]. One-dimensional (1D) semiconductor nanostructures are expected to supply practical components for fururistic electronic, optoelectronic and nano electromechanical systems [2]. The broad direct band gap (3.37 eV) and large excitation binding energy (̴ 60 eV) make zinc oxide (ZnO) an excellent optoelectronic material [3]. ZnO based nanostructure (one-dimensional nanowires/nanorods/nanotubes or two-dimensional nanoplates/nanosheets) because of its various characteristics has a huge attention in the last few years as a multi-functional material like near UV and visible (green, blue and violet) emission, optical transparency, electrical conductivity, piezoelectricity and many other important applications in electroacoustic transducers, gas sensors, Transparent conductive materials used for painting, photovoltaic devices and optical solar cells and other nano devices [4]. In order to focus on this point, the prerequisite for building the nanostructure is the orderly growth in size, shape and orientation, and extensive research has been done to prepare ZnO architectures [5]. Different industrial techniques have been adopted ZnO nanostructures such as vapor transport process or physical vapor deposition (PVD), metal organic chemical vapor deposition (MOCVD), microwave plasma deposition, hydrothermal synthesis and electrochemical deposition [6].

One of the most widely studied is Titanium dioxide (TiO2) transition metal oxide semiconductor and has been rightly applied in solar cells, hydrogen generation, gas sensing, and photo catalysis applications. One of the most common applications is to treat pollution using TiO2 a photo catalyst the effectiveness of TiO2 in these applications is further, Supplemented with its unique properties of non-toxicity cost effective, long-term stability, widely available corrosion stability, and high optical stimulation ability. However, researchers have shown that TiO2 nanotubes are only able to utilize around 2%–3% solar light that reaches the earth due to a large band gap of 3.20 eV. Therefore, the doping of TiO2 nanostructures with transition metals to enable the TiO2; the nanostructure is being extensively researched to respond to a much larger visible area [7].

Method Section:

First Method: By using the spin coating technology, a 250 nm thick ZnO film was deposited as a seed layer. Then, ZnO nanorods were grown on ZnO seed layer by hydrothermal method, at which 100 ml aqueous solution included...
0.05M zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O) and 0.05 M hexamethylenetetramine (C₆H₁₂N₄). To prepare (ZnO:Ga) nanostructure, 4% gallium nitride Ga(NO₃)₃·xH₂O was dissolved in a solution of zinc nitrate hexahydrate and hexamethylenetetramine (HMT).

**Thick film preparation:** Then, at a constant temperature of 150 ºC for 8 hour, the solution transferred to an automatic sealed teflon lined autoclave was kept in the laboratory oven. After the complete reaction, the autoclave cooled down naturally and gradually. Finally, ZnO and ZnO:Ga products grow on FTO coated quartz substrate were dipped carefully in ethanol and stored in air at room temperature. Ohmic contacts were invented by evaporating purity silver nanowires using Edwards coating system. Figure (1) show SEM pictures for silver prepared using hydrothermal method, it can be seen that the morphology of the product is nanowire-like and almost uniform in width (60 ± 10 nm) while the length is in a relatively broad range (from 0.2 to 4 µm) with an average at 2.5 µm.

![Figure (1): SEM of Ohmic contacts (silver NWs) prepared using hydrothermal method.](image)

Titanium foil (99.999%; thickness 0.25 mm) was cut into proper shape for conductive brass in the base holder of a Teflon cell. For 15 minutes the sample was released by sonication with a solution of acetone and ethanol, before anodizing, washed in (DI) deionized water, to remove the mechanical stress and to enhance the grain size the titanium samples were annealed at 550C for 3h and cooled in air. The titanium foil Ti surface was surface polished mechanically with glass papers starting from 240 and increasing to 400, 600, 800 and 1200 with diamond material. And intermittent we polished it with different sanding paper, the surface was washed with (DI) deionized water to remove any particles generated during polishing. Ultrasonic cleaning in acetone, ethanol and (DI) deionized water respectively for about 15 minutes was done after polishing to clean the surface more effectively then dried with (N₂) nitrogen stream, after the mechanical polishing process is completed, sample put in Teflon cell and it is prepared to next electrochemical process. The samples were pressed together with a Cu plate against an O-ring in an electrochemical cell (1 cm² exposed to the electrolyte) and anodized at 25 V in 1M H₂SO₄ electrolytes containing 0.16 M hydrofluoric acid (HF) for 3 h to grow a 600 nm thick TiO₂ nanotube layer. After this, the nanotube layers were rinsed, dried and a second anodization step was performed in 0.09 M NH₄F in deionized water and EG. The water concentration in the solution was 30vol% and the experimental voltage ranged 20, 30, 40, 50, 60 and 70 V for 4 h at room temperature. All electrolytes were prepared from reagent grade chemicals. NH₄F acts as a pore opening reagent and the NH₄F concentration also plays a key role in controlling the surface morphology, but we fixed it into 0.09 M in order to focus on the effects of the water concentration and applied voltage. The TiO₂ nanotube arrays yielded were rinsed with de-ionized water and dried in air spontaneously after the experiments.

The characterizations of semiconductor oxide were examined in Iran using a scanning electron microscope (SEM, FESEM; Hitachi models S-4160, Japan-daypetronic Company) and by Energy Dispersive Spectrometry (EDS).

**Results and Discussion:**

In the figure (2), the Energy Dispersive Spectrometry (EDS), shows the element (Zn and O), the ratio of the Zn to O elements that was quantified equal 89.4:10 as we see in these figures below.
Figure (2): EDS tin and zinc oxide prepared using hydrothermal method

Figure (3) shown the FESEM images with different analargment of ZnO and ZnO:Ga nanostructure. The wurtzite structure of ZnO can be characterization as a pile of a number of alternating planes that are 4-fold coordinated O$_2^-$ and Zn$^{2+}$ ions organize along c-axis. Many of crystal planes exist: the basal plane (0001), one end of this plane is terminated to Zn lattice points and (000Î) plane finished to negative oxygen lattice points. The other six low indices non-polar aspects (Î010 (are parallel to c-axis. The non-polar aspects are energetically most stable and the polar aspects are Interchangeable. The growth rate of various planes follows the growth rule: $V(0001) \leq V(01ÎÎ) \leq V(01Î0) \leq V(01Î1) \leq V(000Î)$. Now the growth rate of (0001) plane is very high and hence it will be disappeared quickly in the experimental synthesis of ZnO, leading to the rod-like structure. More detailed understanding of the growth rate accreditation of different morphologies of ZnO nanostructures is announced by Li et al. (1999). Schematic growths of the nanorods are shown in figure (3).

The calculated of PL spectra for ZnO and ZnO:Ga. shows in Figure (4). They formatted of three peaks centered at 363, 375 and 480 nm respectively. The first peak refers to direct transition of electrons band to band, while the second band UV emission peak related to recombination of free exactions, and the third is the green emission [8].

Figure (3): FESEM images of the growth (ZnO).
As shown in figure (5) (a, b, c and d) the SEM image of TiO$_2$ nanotubes formed on Ti substrate by using anodization method at room temperature. We formed the ordered array of nanotubes with uniform diameter and length. TiO$_2$ is straight, dense and open end with hollow nature of the TiO$_2$ nanotubes. The diameters of these nanotubes ranging from (25-70) nm, retaining the size and near cylindrical shape of the pores.

Energy dispersive spectroscopy (EDX) for TiO$_2$ nanotubes were tested and formed. The EDX spectrum of a TiO$_2$ nanotube attended by using ethylene glycol (EG+deionized water 30 vol%) with ammonium fluoride (NH$_4$F, 0.09 M) deposited on titanium foils by electrochemical anodization is shown in figure (6). The EDX analysis reveals successful formation of TiO$_2$ nanotubes and also can be proven that by the measurement of X-ray diffraction (XRD) patterns as in Figure (3). The major components of the TiO$_2$ nanotube are titanium and oxygen with compound percentage for the (Ti) and (O) are 65.1:34.9 respectively.

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**Figure (4): PL of zinc oxide nanostructure.**

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**Figure (5): SEM of TiO$_2$ nanotube.**
From figure (7) we can see the characteristic XRD patterns for TiO$_2$ nanotube arrays on Ti foil by anodization method. TiO$_2$ standard nanotubes powder their diffraction pattern and their relative density contains consistent peak positions. It was appeared that all of the peaks can be mention to the polycrystalline TiO$_2$ with different phases were concord through the electrochemical anodic oxidation.
Figure (7): XRD of TiO$_2$ nanotube arrays fabricated by anodization method
Conclusions

The ZnO nanorods vertically aligned grown on FTO coated quartz substrates using hydrothermal method. The element ratio of Zn to O is quantitatively calculated equal 89.4:10.6, further confirms the high purity of ZnO nanomaterials.

TiO$_2$ nanotubes grown on Ti foil by using hydrothermal and anodization method. TiO$_2$ is straight, dense and open end with hollow nature of the TiO$_2$ nanotubes. The diameters of these nanotubes ranging from (25-70) nm, retaining the size and near cylindrical shape of the pores. The major components of the TiO$_2$ nanotube are titanium and oxygen with compound percentage for the (Ti) and (O) are 65.1:34.9 respectively. The peak positions and their relative intensities are consistent with the standard powder diffraction pattern of TiO$_2$ nanotube.

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