Ferroelectric Photodiode Based on BaTiO$_3$ Nanorods Film

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Abstract: The photodiode e of BT/Si film has successfully fabricated by growing BT on the surface of the p-type Si (100) substrate using the hydrothermal method. BT films were made after preparing TiO$_2$ film and deposited on a Si substrate via screen printing method. The structural, optical, electrical properties of the fabricated films were done. The morphology and distribution of the BT nanoparticles were homogenous and in the form of nanorods of 1.5 micron height through FESEM image. The I-V characteristic was conducted in dark and illuminate conditions with a Xenon lamp. The crystallite D size and strain were calculated using the Williamson Hall plot of BT film. The band gap of BT film is calculated using the Tauc and reflection method. The value of the energy gap extracted using the reflection method was greater than it was when using the Tawc method. The dark and (b) illuminated (J-V) characteristics have measured under simulated AM1 conditions for a BT/Si photodiode. The BT/Si film begins to become more conductive when illuminating power density increased, which qualifies the film for photovoltaic applications.

Keywords: Screen printing, TiO$_2$ nanorod, BaTiO$_3$, Hydrothermal, photodiode.

1. Introduction

In recent times, the demand for ferroelectric materials has increased due to the unique properties they offered, especially the ferroelectric thin films, which have attracted many researchers to include these materials in photovoltaic applications and solar cells [1-3]. Where these ferroelectric materials such as barium titanate (BT) have a high polarization, which increases their consistency of selecting on the basis that they possess the internal building voltage that required in such applications [4-6]. One of the most important characteristics of ferroelectric materials is that they have a high dielectric constant and a low...
dielectric loss factor, which increases the chances of them being used as high storage capacity, dynamic random access memory, pyroelectric detector, and filters [7, 8].

In the present paper, it has prepared TiO2 film deposited on Si substrate using the screen printing method. In the next step, the hydrothermal process using to prepare BT/Si film. In this work, BT film deposited on Si substrate was used to explore the photocurrent response. The aim of this work was to study the structural, optical, and electrical properties of the BT film. The prepared films were characterized by XRD, FESEM, UV-Vis spectroscopy, and photocurrent diode.

2. Experimental

A chemical etching of Si-wafer (1.5 x 1.5cm) has been done by HF acid diluted with deionized water (1:10) for 20 min to remove the oxide layer from the surface of the silicon. The details of the process of screen printing and making a titanium dioxide film are similar working as Salman et al [9]. A 12.6 gm of barium hydroxide was dissolved in 100 ml of distilled water at a temperature of 90 °C. In another step, the resultant solution was added to autoclave that containing a titanium oxide film deposited on the silicon substrate and then placed in the oven at 140 °C for two hours. After that, the sample was taken out, cooled, and washed several times with distilled water.

The structural properties of BT film was studied using the X-ray diffraction (shimadzu X-Ray Diffractometer XRD 6000), while the optical properties was measured using a UV-Visible Spectrophotometer (UV-1800, shimadzu). The SEM was used to study the morphology, distribution and morphology of particles deposited on the membrane. The reflection of the film was measured using optical spectroscopy (avantes Avalight –DH-S-BAL) within the wavelength range of (240-1300 nm).

3. Results and discussions

Fig. 1 exhibits the XRD pattern of BaTiO3 thin film formed after reacting Ba(OH)2 with TiO2 film that was deposited on the Si substrate using hydrothermal method at 140°C for 2 h. Fig. 1 confirmed the TiO2 phase is almost completely transformed into the BaTiO3 phase after immersion TiO2 film inside autoclave that containing 0.4 mol/L of Ba(OH)2 for 2 h. The BT films showed to have good crystallinity and agreement with BaTiO3 ferroelectric tetragonal phase ICDD No. 05-0626. Two peaks belonging to TiO2 (Anatase) are observed in Fig 1. (ICDD No. 021-1272) this approved there is a small amount of unreacted TiO2, which can be attributed to TiO2 film is needing extended reaction time to complete converting to BT or could be caused by the thickness of the BT film formed was very small. It is possible to extend the reaction time to obtain a homogeneous BT film or to increase the concentration of barium
hydroxide and it is also possible to increase the reaction temperature during the hydrothermal process to satisfy the grain growth formation. According to published researches, the results of the X-ray diffraction of the tetragonal titanium barium confirmed the splitting of the peak corresponding to 200 plane that matched with 2θ equals to ~ 45 degree [4], Fig. 1 does not show any split of the indicated peak, but it is clear that there is a broadening of it.

![XRD pattern of BT film prepared by hydrothermal method.](image)

**Figure 1.** XRD pattern of BT film prepared by hydrothermal method.

Fig. 2 shows the plot of Williamson Hall [10] of TiO$_2$ and BT films respectively. The crystallite size and strain of the BT film are 22.86 nm and 0.00145 according Williamson Hall plot.
Fig. 3 shows FESEM images with cross-sectional of TiO2 films deposited on FTO substrates. The morphology of the TiO2 film contains irregularly columnar with a reduced visible void by merging in the lateral direction. The underlying FTO substrates can be recognized by darker coloration, while the TiO2 film show densely rods packed decorated with remarkably small granular features on the order of 20 nm. It is noted from the cross-sections film (Fig 3 b) that the thickness of the TiO2 film was approximately 1 μm. After treated TiO2 film hydrothermally at 150°C for 2 h, the BaTiO3 film has formed and the FESEM image is shown in Fig. 4.
**Figure 3.** (a) FESEM images of TiO2 films deposited on FTO substrates. (b) cross section of TiO2 films.
Figure 4. (a) FESEM images of BaTiO₃ films deposited on FTO substrates. (b) Cross section of BaTiO₃ films.
The transmission spectra of the TiO2 and BT films are shown in Fig 5. The TiO2 film was highly transparent in the visible region than that of BT film, this is clear from the flat region shown in Fig. 5.

The optical indirect band gap was determined using the Tauc method. The band gap was extrapolated from the absorption edge to the x-axis of the plot $(\alpha h\nu)^{1/2}$ versus $h\nu$. Fig. 6 displays the band gap of TiO2 and BT films respectively. The band gap of the TiO2 film decreased from 3.32 eV to 2.84 eV after BT film formed as shown in Fig. 6.

![Figure 5. UV-VIS optical transmission spectra of a) TiO2 film, and b) BT film](image-url)
Fig. 7 shows the reflection spectra and energy band gap of BaTiO$_3$ film. The energy gap value was extracted using reflection data, and this method was used in detail by the researcher Kumar et al.[11]. The energy gap value measured using the reflection method (3.07 eV) of the BT film prepared by the hydrothermal method showed slightly greater than when using the Tauc method (2.84 eV) as shown in Fig. 7.

Figure 6. Energy gap of a) TiO2 and b) BT film.

Figure 7. a) Reflection spectra of BaTiO$_3$ film, b) Energy band gap of BaTiO$_3$ film.
The emission spectra of BaTiO3 film prepared by the hydrothermal method is shown in Fig 8. The emission spectra of BT film is conducted under excitation at 394 nm as indicated in Fig. 8. The spectral were ranged from 750 nm to 800 nm showed peak centered at 775 nm. Figure 9 shows the Hall voltage of the BT film, where it showed that the Hall voltage is negative and increases linearly with the current. The conductivity of the BT film as a function of reciprocal temperature is plotted in Fig 10. The lack of observation of the change that occurs due to the Curie temperature in the Fig 10 can be attributed to the small particle size of the BT film, which causes the absence of ferroelectric properties.

![Emission spectra of BaTiO3 film.](image)

**Figure 8.** Emission spectra of BaTiO3 film. Excitation wavelength was 387 nm.
Figure 9. The relationship between Hall Voltage (VH) and passing current for BaTiO3 film.

Figure 10. Conductivity as a function of temperature for BaTiO3 film.

Figure 11 (a) shows the dark and (b) illuminated (J-V) characteristics under simulated AM1 conditions for a BT/Si photodiode. The result confirmed that the film was sensitive to light due to a shift in the curve that occurred when the voltage was given from -8 volt to +8 volt with dark and illumination conditions. The increase in current when illuminated is very large compared to that when it is dark because the films became more conductive. This response qualifies the film for solar cell applications.
Figure 11. (a) Dark and (b) illuminated (J-V) characteristics under simulated AM1 conditions for a BT/Si photodiode.

Figure 12 shows I-V curves with a dark and illuminating power density from 20- to 80 mW / cm2 of BaTiO3 / Si photodiode under reverse bias. Obviously in Fig 12, as the illuminating power density increases, the photocurrent density increases accordingly, which confirms the possibility of using the film in photovoltaic applications. The properties of the BT/Si film are affected by the absorbed photons by the electrons that available in the conductive film, as there is a possibility for the photons to diffuse these electrons, which results in the re-union of electrons with increasing holes.
Figure 12. Illuminated (J-V) characteristics of BaTiO3/Si photodiode under Reverse Bias for various illuminating power densities.

4. Conclusion

BT film has successfully been deposited on Si substrate by hydrothermally treated of TiO2 film for 2 hours at 140°C. The energy gap of the BT film showed that it was in the range of semiconductors value. The structural, optical, electrical properties of the BT film was performed. The I-V characteristic was measured in dark and illuminate conditions with a Xenon lamp. The studied electrical properties of the prepared film showed the possibility of using prepared film as a photodiode.
5. References

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