Synthesis and characterization of silver nanoparticles-doped titanium (IV) oxide thin films

SW Balogun*1, AB Abdulhamid2, YK Sanusi1,3, and O Adedokun3

1Department of Physics and Materials Science, Kwara State University Malete, Ilorin, Nigeria
2Department of Physics, School of Science, Kwara State College of Education, Ilorin, Nigeria.
3Department of Pure and Applied Physics, Ladoke Akintola University of Technology, Ogbomoso, Nigeria

*Corresponding author: Sunday Wilson Balogun (sbalogun94@gmail.com)

Abstract

Current advancements in nanotechnology appear to open a more efficient, stable, and cheaper way of producing solar cells to replace the too expensive means of inorganic solar cells production. The creation of nanoscale materials for advanced structures has led to a growing research interest in the area of photovoltaic energy conversion using photovoltaic devices. This research investigates the impact of annealing temperature on the optical properties of silver nanoparticles-doped titanium (IV) oxide thin film (TiO2:AgNPs) deposited by spin-coating method on glass substrate. AgNPs were prepared using the leaf extract of Gliricidia sepium as a reducing agent for silver nitrate. Deposition of TiO2:AgNPs composite solution was performed in different volume ratio. Deposition of TiO2:AgNPs volume ratio (1:0.2) was performed with different spin-coating speed for 30 seconds at 7 different thicknesses. Characterization of the optical properties of thin films was carried out by using a UV-vis single beam spectrophotometer; this was used to calculate the absorbance and the bandgap energy. Sixteen 16 samples of TiO2:AgNPs deposited at 1000 rpm on the glass substrate were annealed at temperature range of 50 to 425 °C with step of 10 °C interval in a tubular furnace. It was observed from the results that the peak absorption of photon energy occurred at 375 °C in the visible spectrum of the wavelength band. The optimal thickness for peak absorbance of the TiO2:AgNPs blend layer occurred at 115 nm in the visible spectrum and at the corresponding spin speed of 1000 rpm. The optimized fabrication process with blend layer thickness of 115 nm
yielded the best absorbance at an annealed temperature of 375 °C in the visible spectrum. The volume ratio of (1:0.2) gave the peak absorption at 0.75 au. At 1000 rpm with the corresponding thickness of 115 nm, TiO₂:AgNPs blend has the peak absorbance. The energy band gap of the blend thin film is 3.58 eV at 375 °C in the visible spectrum of wavelength band. The result obtained showed that AgNPs enhanced light absorption, broadened absorption spectral range and thermal stability of titanium (IV) oxide film. The result can be used as a guideline in the design and fabrication of solar cells.

Keywords: Organic thin film; silver nanoparticles; titanium dioxide; annealing; blend AgNPs:TiO₂; optical properties

1. Introduction

Demand for eco-friendly and clean energy has increased in recent times leading to increase in research towards alternative source of energy and development of solar energy. Researchers have focused attention on nanotechnology which is an arm of science and technology that deals with different materials at a nanoscale. Nanotechnology involves production, manipulation and use of materials at subatomic level that finds its application in materials science, engineering, electronics, photovoltaics, biological, and chemical sensors [1-23]. Silver nanoparticles uniqueness is found in its optical, electrical, and thermal stability. Silver nanoparticles characteristics include low sintering temperatures, high electrical conductivity and stability. Silver nanoparticles can be prepared using the following methods: ultrasound, anodization, co-precipitation, sol-gel method, chemical vapor deposition and mechanochemical-thermal synthesis [24-27]. This research investigates effect of annealing temperature on the optical properties of silver nanoparticles doped titanium (IV) oxide (TiO₂:AgNPs) thin films deposited by spin-coating method on glass substrate.

2. Materials and Methods

2.1. Preparation of thin films of TiO₂:AgNPs

Titanium (IV) oxide nanopowder (< 35nm), 97% purity was purchased from Sigma-Aldrich Company (USA), while silver nitrate and other chemical reagents were purchased locally. The glass substrates of dimension 25.4 mm by 76.2 mm were washed with liquid detergent in ultrasonic sonicator for 10 to 15 min and then rinsed in distilled water for 15 min at 27 °C. The
substrates were further cleaned with isopropanol alcohol (IPA) in ultrasonic bath for 15 min at 27 °C and dried in a stream of nitrogen gas (N₂). To prepare TiO₂, 25ml of ethanol was added into 3 g of TiO₂ powder. The solution then underwent ageing process for 3 h at room temperature without heat to allow homogeneous mixture and TiO₂ powder to fully diffuse into the solvent. Ethanol was chosen as a solvent because it has no characteristic absorption and emission in the visible spectrum of wavelength band. Then, 0.168 g of silver nitrate was dissolved in 100 ml deionized water which gives colorless clear solution.

Then, 3 g of leaves of *Gliricidia sepium* were thoroughly washed, rinsed and cut into pieces. Thereafter, the pieces of leaves were immersed in 300 ml of boiling distilled water for 30 min and followed by filtration. The filtered extract was dissolved into 100 ml of 0.01M of aqueous silver nitrate solution and stirred for homogenous mixture. The product was stored in a brown bottle shielded from the ray of light. Blend solution (TiO₂:AgNPs) was done by mixing TiO₂ solution with AgNPs solution at different composite ratio (1:1, 1: 0.8, 1: 0.6, 1: 0.4, 1: 0.2) and stirred using magnetic stirrer for homogeneous mixture. TiO₂ solution was deposited on glass substrate as reference (control sample), while the blend solution of TiO₂:AgNPs were deposited at 5 different volume ratio (1:1, 1: 0.8, 1: 0.6, 1: 0.4, 1: 0.2) ml using spin-coater (Laurel WS-650Hz-23NPP).

The blend solution with volume ratio of (1:0.2) ml has highest absorption value after optical properties characterization. This optimized absorption TiO₂:AgNPs (1: 0.2) volume ratio was used to deposit another seven films of layer thicknesses of 30 nm, <35nm, 35 nm, 87 nm, 98 nm, 115 nm, and 146 nm corresponding to spin coating speeds of 4000, 3000, 2000, 1500, 1250, 1000, and 750 rpm, respectively for 30 seconds on glass substrate. Depending on the speed of rotation of the spin coater, the desirable thickness of the sample was obtained. It is important to note that the thickness of film being spin-coated depend on both time and speed of rotating stub as specified by equipment manufacturer. Another method of determination of thickness is by using Equation (1) in the absence of surface profilometer.

\[
t = \frac{M_2-M_1}{AD}
\]

Where \( t = \text{thickness (nm)} \), \( M_1 = \text{mass of substrate before deposition} \), \( M_2 = \text{mass of substrate after deposition} \), \( A = \text{Area covered by the film} \), \( D = \text{Density of the material} \).
The fabricated TiO$_2$:AgNPS at 1000 rpm with corresponding thickness of 115 nm, has best absorption value after optical properties characterization. At the deposition rate of 1000 rpm seventeen sample films were prepared and annealed at temperature range of 50 to 425 °C with 10 °C interval in a carbolite tubular furnace (model Srw 21-501042 Type-CT17) for 30 min. One sample was used as a reference.

2.2 Characterization

The TiO$_2$ solution and synthesized AgNPs thin films prepared on clean glass substrates by spin-coating method were characterized using UV-vis spectrophotometer (Avantes, Avalight-DH-5-BAL) to determine the absorption values in arbitrary unit (au) and spectrum using the recorded transmittance and reflectance (%). Absorbance was calculated using Equation (2)

\[ A = 2 - \log(\%T)_{au} \]  

Where A is the absorbance, \%T is the percentage transmittance.

The wavelength band for which a material absorbs photon energy and convert it to electricity helps determine whether the material is capable of converting the available light illuminating it into electric energy. Absorption was chosen as the optimization variable because the choice of layer thickness is a function for optimization of the efficiency.

(i) Graph of absorption against photon energy

Photon energy values were determined from the inverse relationship between energy in electron volts (eV) and wavelength of the UV-visible spectrum using equation (3).

\[ E = \frac{hc}{\lambda q} \text{(eV)} \]  

Where \( E \) = Photon energy, \( h \) = planck’s constant, \( C \) = speed of light, \( \lambda \) = wavelength in nanometres (nm), \( q \) = electronic charge, 1 eV = 1.6×10^{-19} J

3 Results and Discussion

The absorbance readings of TiO$_2$ (control) and TiO$_2$ loaded with AgNPs prepared at different composite ratio are as shown in Figure 1a. The blend solution with composite ratio of (1:0.2) ml has the highest absorbance (au) and this optimized volume ratio was then deposited at different spin-coating speeds of 4000, 3000, 2000, 1500, 1250, 1000, and 750 rpm in Figure 1b. Thermal
annealing was carried out on all the samples as shown in Figures 1c and 1d. The optimized film thickness for peak absorbance of the TiO$_2$:AgNPs blend layer occurred at 115 nm in the visible band of spectral and at the corresponding spin speed of 1000 rpm. The optimized fabrication process with blend layer thickness of 115 nm yielded the best absorbance at annealed temperature of 375 °C in the visible spectrum as shown in Figures 1c and 1d. The graph of the plot of absorbance versus photon energy in eV of TiO$_2$:AgNPs is shown in Figures 1e and 1f. The energy band gap of the blend thin film is 3.58 eV at 375 °C in the wavelength range of visible light. The result also revealed that heat treatment or thermal annealing is a tool that can be used to tune the optical properties of TiO$_2$:AgNPs blend thin film.

![Graphs](graphs.png)

**Figure 1.** Absorbance of TiO$_2$ and blend TiO$_2$:AgNPs (a), TiO$_2$:AgNPs (1:0.2) at different layer thicknesses (b)
Figure 1. TiO$_2$:AgNPs at different annealing temperature (c), TiO$_2$:AgNPs (1:0.2,1000 rpm) at selected annealing temperature (d)

Figure 1. Graph of absorption vs. photon energy (e), the slanting line at 375 °C (f)

4. Conclusion

The result obtained showed that gradual thermal annealing, in a controlled manner revealed a more stable and efficient control in tuning the TiO$_2$:AgNPs thin films. The results can form a guideline to design and fabricate solar cells. Results obtained could lead to a breakthrough in performance improvement and stability of solar cells.
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