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Structural and Optical Properties of TiO_2@Cu_2O Thin Film

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***Abstract*— The Cu_2O thin film was deposited onto spin coated TiO_2 thin layer by electro-deposition method. The crystallographic structure of the thin film was studied by X-ray diffraction (XRD). XRD measurement showed that the film was crystallized in the cubical phase and the average crystallite size was found to be 72.317 nm. The grain size of the thin film was studied by scanning electron microscope (SEM). The SEM showed that the TiO_2@Cu_2O array consisting of cylinder shaped nanowires which have small feature sizes (an average diameter of ~ 90 nm and a typical length of ~ 2 µm). Optical properties such as refractive index (n) and extinction coefficient (k) were determined from transmittance spectrum with SHIMADZU UV-1800 spectrophotometer by using envelope method. Absorption coefficient (α) and the thickness of the film (t) were calculated from interference of the transmittance spectrum. The energy band gap and the thickness of the TiO_2 @ Cu_2O thin film was evaluated to be 2.81 eV and 0.709 µm.**

Keywords*— TiO_2@Cu_2O; XRD; SEM; SHIMADZU UV-1800; envelope method.

I. INTRODUCTION

Semiconductor nanowires are promising for photovoltaic applications, but, so far, nanowire-based solar cells have had lower efficiencies than planar cells made from the same materials, even allowing for the generally lower light absorption of nanowires. The core-shell geometry of nanowires is thought to be able to enhance the efficiency of charge collection by shortening the paths travelled by minority carriers. An ideal core-shell configuration is highly desirable for its low recombination rate and high collection efficiency [1,2,3]. Titanium oxide (TiO_2) has been one of the most studied oxides because of its role in various applications, namely photo induced water splitting, dye synthesized solar cells,solar cells environmental purifications, gas sensors, display devices batteries etc[4]. Cuprous oxide (Cu_2O) has the advantages of low consumption, nontoxic, and higher conversion efficiency. Therefore, it is widely used in solar cells, lithium ion batteries, biological sensors, gas sensors, magnetic storage, microdevices, and negative electrodes[5]. The crystal structure of the thin films were examined by X-ray diffraction (XRD). The morphology of the nanostructure of the thin films were investigated by scanning electron microscopy (SEM). The UV-visible absorption or transmission spectra were obtained using SHIMADZU UV-1800 spectrophotometer. The envelope method was used to analyze transmission spectra with peaks and valleys induced by interference effects in thin films for evaluating their optical constants: refractive index n (λ), absorption coefficient α (λ) and extinction coefficient k (λ)[6,7,8].

II. PREPARATION OF TIO2@CU2O CORE-SHELL THIN FIMN

2g of TiO_2 powder and 20ml of methanol were mixed in the beaker. Then, it was annealed 110 ºC for 1 h with water bath. Next, this solution was continuously stirred by a magnetic stirrer for 1.5 h with 600 rpm to be homogeneous. After stirring, TiO_2 solution was be formed. Firstly, ITO coated glass substrate was wet-cleaned with acetone and deionized water about 10 min. The substrate was subsequently baked at 80 ºC for 10 min to evacuate moisture. TiO_2 solution was then deposited onto the glass substrates by spin coating with 1000 rpm for 5 min. These sample was annealed at 500ºC for 1 h. Thus TiO_2 thin film was to be formed. 0.2 g of Copper (II) sulphate (Cu_2SO_4) and 25 ml of deionized (DI) water were mixed and aged with pH-3 for 10 min. Next 6 ml of Lactic acid ($C_3H_6O_3$) and 25 ml of DI water were also mixed and aged with pH-1 for10 min. 4 g of sodium hydroxide (NaOH) and 25 ml of DI water were mixed and aged with pH-14 for 10 min. The above three samples were mixed and stirred by magnetic stirrer at 700 rpm for 1 h with pH-10. The sample prepared by electrochemical deposition method was made to dissolve in DI water. Then, this solution was deposited onto glass substrate by electrochemical deposition method. Firstly, this mixture solution was treated as bath temperature at 100 °C for 1 h. TiO_2 thin film substrate was placed into plating solution and connected it to the cathode of power supply. The copper plate was placed into plating solution and connected it to the anode of power supply. Parameter that affects the electroplating process was used to 5 volts in 1 h. It was annealed at 150 °C for 30 min. Finally TiO_2@Cu_2O core-shell thin film was to be formed.

III. RESULTS AND DISCUSSION

XRD analysis

Figure 1 showed the XRD pattern of TiO_2 @ Cu_2O core-shell thin film. Form XRD plot, almost reflections were well-matched with the diffracted peaks of standard anatase TiO_2 and Cu_2O. The TiO_2 peaks were found to be (1 0 1), (1 0 3), (0 0 4), (2 0 0), (2 0 2), (2 0 2), (1 0 5) and (2 1 1) planes. The Cu_2O peaks were found to be (1 1 1), (2 0 0), (2 1 1), (2 2 0), and (3 1 0) planes. The average lattice parameter of a-axis for TiO_2 @

Cu_2O thin film was observed as 5.166 Å. The average crystallite size was observed 72.317 nm.

SEM investigation

The SEM image (Inset in Figure 2) shows that the nanowires have a core–shell structure of $TiO_2@Cu_2O$ thin film. The $TiO_2@Cu_2O$ array consisting of cylinder shaped nanowires which have small feature sizes (an average diameter of ~90 nm and a typical length of ~2 μm). The position of nanowires were horizontally and vertically aligned and uniform distribution in this SEM image. The wires are in direct contact with the substrate, with no intervening TiO_2 particles layer.

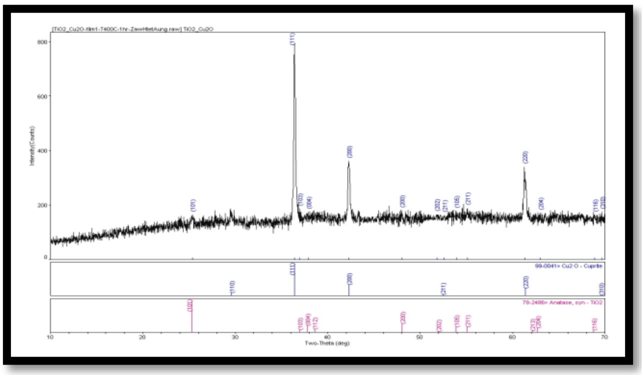

Figure 1 XRD pattern of TiO_2 @ Cu_2O core-shell thin film

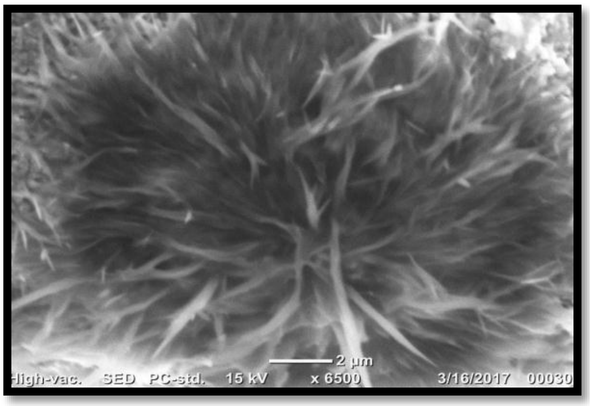

Figure 2 SEM image of TiO_2 @ Cu_2O core-shell thin film

UV-Vis analysis

The absorption peaks of $TiO_2@Cu_2O$ core-shell thin film are 325.00 nm, 345.00 nm, 373.00 nm, 392 nm 407.00 nm 433.00 nm and 569.00 nm. All absorption peaks of $TiO_2@Cu_2O$ core-shell thin film are also observed in the UV range. Figure 2.33 showed UV-Vis transmission spectrum of $TiO_2@Cu_2O$ core-shell thin film. The transmission peaks of $TiO_2@Cu_2O$ core-shell thin film are 421.00 nm, 453.00 nm, 482.00 nm, 507 nm, 547.00 nm and 576.00nm.

The widely used enveloped method has been developed for transmittance measurements to evaluate the refractive index, extinction coefficient and absorption coefficient. The optical band gap (E_g) and absorption coefficient (α) could be evaluated from transmittance or absorbance spectra [9,10].

An excellent surface quality and homogeneity of the film were confirmed from the appearance of interference fringes in the transmission spectrum occurring when the surface of film is reflecting without much scattering/absorption in the bulk of the film. The optical constants were evaluated using the envelope method originally developed by Manifacier et al. The optical measurements of the TiO_2 thin films were carried out at room temperature using SHIMADZU UV-1800 spectrophotometer in the wavelength range from 300 nm to 900 nm. Swanpoel's envelope method was employed to evaluate the optical constants such as the refractive index (n), extinction coefficient (k), and absorption coefficient (α) from the transmittance spectrum [11].

The thickness of the film was calculated using the following relation:

$$t = \frac{\lambda_1 \lambda_2}{2[n(\lambda_1)\lambda_2 - n(\lambda_2)\lambda_1]} \quad (1)$$

Where n (λ_1) and n (λ_2) are the refractive indices at the two adjacent maxima (or minima) at λ_1 and λ_2. When TiO_2 @ Cu_2O thin film thickness were calculated by using equation (2.12), the thickness of TiO_2-@Cu_2O Core-shell thin film was found to be 0.709μm.

The optical constants such as refractive index (n) and extinction coefficient (k) were determined from a transmittance spectrum by using envelope method. The refractive index can be calculated from the following equations:

$$n = [N + (N^2 - n_s^2)^{\frac{1}{2}}]^{\frac{1}{2}} \quad (2)$$

$$N = \frac{(n_s^2 + 1)}{2} + 2n_s \frac{(T_{max} - T_{min})}{T_{max} T_{min}} \quad (3)$$

Where n_s is the refractive index of the substrate (n_s = 1.52 for glass), T_{max} and T_{min} are maximum and minimum transmittances at the same wavelength in the fitted envelope curves on the transmittance spectrum. The extinction coefficient can be also calculated by the following equations:

$$k = \frac{\alpha\lambda}{4\pi} \quad (4)$$

$$\alpha = \frac{1}{t} \ln \frac{(n-1)(n-n_s)(\frac{T_{max}}{T_{min}} + 1)^{\frac{1}{2}}}{(n+1)(n-n_s)(\frac{T_{max}}{T_{min}} - 1)^{\frac{1}{2}}} \quad (5)$$

Where α is the absorption coefficient and t is the film thickness. λ_1 and λ_2 are the wavelength at the two adjacent maxima or minima .The variations of refractive index (n) as the function of wavelength for thin film was showed in the Figure 3. The refractive index of the thin films was exponentially decreased with the wavelength. The extinction coefficient (k) of the thin films was proportional increased with wavelengths as shown as Figure 4. The absorption coefficient (α) of thin film was determined from transmittance measurement. Since the envelope method is not valid in the strong absorption region, the calculation of the absorption coefficient of the film in this region was performed using the following expression:

$$\alpha(\nu) = -\frac{1}{t}\ln(T) \qquad (6)$$

Where T is the normalized transmittance and t is the film thickness). These absorption coefficient values were used to determine optical energy gap. Figure 5 showed the plot of $(\alpha h\nu)^2$ versus hν for the thin films, where α is the optical absorption coefficient and hν is the energy of incident photon.

The energy bap (E_g) was estimated by assuming a direct transition between valence and conduction bands from the expression .

$$\alpha h\nu = K(h\nu - E_g)^{1/2} \qquad (7)$$

Where K is a constant, The band gap (E_g) was determined from each film by plotting $(\alpha h\nu)^2$ versus hν and then extrapolating the straight line portion to the energy axis at $\alpha = 0$. The band gap energy E_g was obtained for each thin film. From this drawing, the optical band gap E_g = 2.81 eV was deduced for the $TiO_2@Cu_2O$ core-shell thin film.

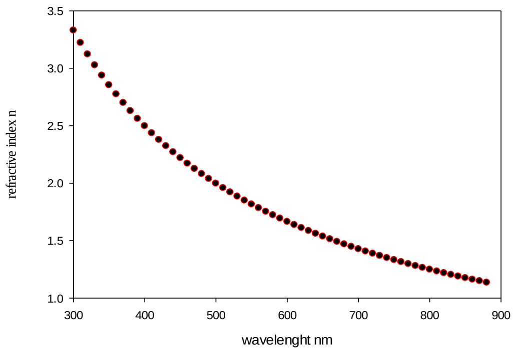

Figure 3 Plot of refractive index (n) as a function of wavelength of $TiO_2@Cu_2O$ core-shell thin film

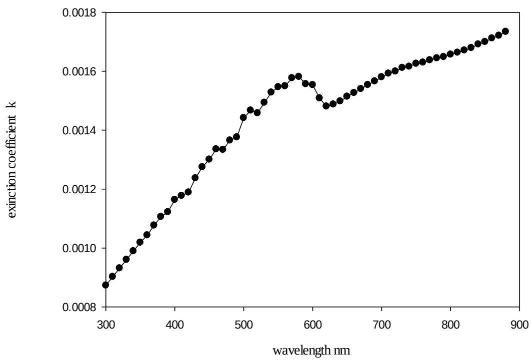

Figure 4 Plot of extinction coefficient (k) as a function of wavelength of $TiO_2@Cu_2O$ core-shell thin film

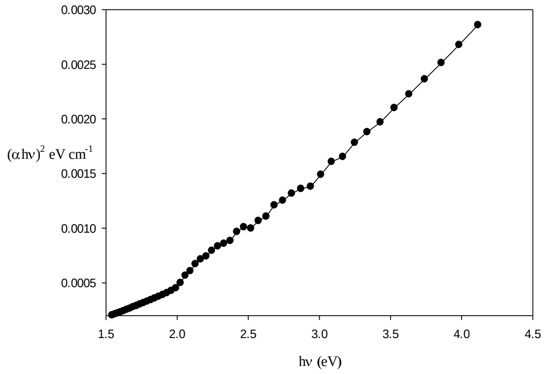

Figure 5 Plot of $(\alpha h\nu)^2$ versus hν for $TiO_2@Cu_2O$ core-shell thin film

IV. CONCLUSION

The Cu_2O thin film was deposited onto spin coated TiO_2 thin layer by electro-deposition method. The crystallographic structure of the thin film was studied by X-ray diffraction (XRD). XRD measurement showed that the film was crystallized in the cubical phase and the average crystallite size was found to be 72.317 nm. The grain size of the thin film was studied by scanning electron microscope (SEM). The SEM showed that the $TiO_2@Cu_2O$ array consisting of cylinder shaped nanowires which have small feature sizes (an average diameter of ~90 nm and a typical length of ~2 μm). UV-Vis absorption and transmission values of TiO2@Cu2O core-shell thin film was measured in (Shimadzu UV-1800) spectrophotometer. The refractive index of the thin film was exponentially decreased with respect to the values of wavelength. The extinction coefficient (k) of the thin film was proportional increased with wavelengths. The energy band gap and the thickness of the TiO_2 @ Cu_2O thin film was evaluated to be 2.81 eV and 0.709 μm. Accordingly, it is confirmed that $TiO_2@Cu_2O$ core-shell thin film is quite promising candidate for photovoltaic and solar cell devices. The research done is said to be non-expensive, technically simple and easily acceptable.

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