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Chemically Deposited Cuprous Oxide Thin Film on Titanium Oxide for Solar Applications

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Abstract

Semiconducting cuprous oxide film (shell) was prepared by chemical bath method onto chemically bath deposited Titanium oxide thin film (core). The deposited films were treated under various annealing temperature up to 673K in order to determine the effects of thermal annealing on the structural and optical properties of the film. Our results showed that there is more crystallization and more orientation of the crystal growth with increase in temperature. TiO_2/Cu_2O core/shell thin film has α in the range of 0.8 – 3.5 m^{-1}. The optical band gap lies between 2.99eV- 4.00eV. The properties indicates that the thin film can be used as coatings for suppression of UV radiations, in thermal control and solar control coating, electrical isolation and so on.

Keywords: chemical bath deposition, Thin films, Annealing, Bandgap, optical-properties, Core/shell, Refractive- index, Scherer formula, Grain size.

1. Introduction

Thin films of TiO_2 and Cu_2O oxide film are some of the metal oxide semiconductors which have been found to be very useful as a UV detector .[1] As important group II-IV semiconductor thin films with versatile characters, these films possess wide applications in various field: such as gas sensors, transducers, catalysis, secondary batteries and super capacitors. [2] In recent years, the development of core/shell structured materials on a nanometre scale has been receiving extensive attention [3,4]. The shell can alter the charge, functionality, and reactivity of surface, or improve the stability and dispersive ability. Furthermore, catalytic, optical, or magnetic functions can be imparted to the core particles by the shell material. In general, the synthesis of core/shell structured material has the goal of obtaining a new composite material having synergetic or complementary behaviours between the core and shell materials. Many studies on the synthesis of composites, i.e. TiO_2 [5], $CaCO_3$ [5,6], Fe_2O_3 [7] and Ag coated with SiO_2 shells have been reported.

In this communication, we report the synthesis of TiO_2/Cu_2O thin film. in a PVA matrix via simple and inexpensive chemical both deposition technique. We also present the effect of post deposition annealing on properties of the deposited films.

2. Methods

The chemical bath used for the preparation of the thin films in PVA matrix in this work was prepared in the following order. First the PVA solution was prepared by adding 900ml of distilled water to 1.8g of solid PVA and stirred at 363K for 1hr. The solution was aged until the temperature dropped to room temperature. To obtain the deposition of TiO_2, the chemical bath was composed of 12mls of 1M $TiCl_3$, 12mls of 1M $NH4Cl_4$, 12mls of 10M NH_3 and 13mls of PVA solution put in that order in 100ml cleaned and dried beaker. Three (3) clean glass slides were then inserted vertically into the solution. The deposition was allowed to proceed at a temperature of 338K for 3hrs in an oven after which the coated substrate were removed, washed with distilled water and allowed to dry. To obtain the TiO_2/Cu_2O core-shell, the TiO_2 already formed (core) was inserted in a mixture containing 24mls of 1M of $CuSO_4$, 24mls of 10M of NaOH solution and 13mls of H_2O and were allowed to react in the reacting bath for 3 hours at a temperature of 348K. Thereafter the slides were withdrawn washed with de-ionized and distilled water and allowed to dry.

3. Results and Discussion

Structural analysis of the films was carried out using X-ray diffraction (XRD) method within the range of 15- 75^0 on a computer controlled Phillips pin 1500 X-ray diffractometer of CU-Kα wavelength (1.5408Å). The composition of the films was determined using Rutherford back scattering (RBS) ,while the optical properties of the CBD deposited films were measured at room temperature from Unico-UV-2102PC Spectrophotometer at normal incident of light in the wavelength range of 0-1500nm. From the absorption spectra, optical band gaps of the samples were determined. The crystalline grain size was calculated using the Scherrer formula [8]

$$D=0.89\lambda/\beta\cos\theta \qquad (1).$$

Where D is the average crystalline size, λ is the wavelength of the incident X-ray, β is the full width at half maximum of X-ray diffraction and θ is the Bragg's angle. The thickness of the samples of the deposited film was calculated using the formula [9]

$$t = \frac{\lambda_1 \lambda_2}{2(n_1 \lambda_2 - n_2 \lambda_1)} \quad (2)$$

Where n_1 and n_2 are the refractive indices corresponding to wavelength λ_1 and λ_2 respectively. The values of the thickness of the samples are displayed in table 1.

The chemical status and the elemental composition of the film was analysed by using RBS. The result showed that the film contained 10.1% of titanium, 30.2% of copper and 68.9% of oxygen.

Fig.2a, b and c show the XRD patterns of TiO_2/Cu_2O samples for as-deposited, thermally annealed at 373K and 673K respectively. Peak broadening has been observed in recorded diffraction pattern of the crystalline thin films. Comparison, among the pattern of (a), (b), and (c) show that there is more crystallization and more orientation of the crystal growth in the case of the film annealed at 673K. The lines become stronger with slight preferential orientation at ($2\theta = 25.3398^0$) that corresponds to (111) plane, and at ($2\theta = 68.76^0$) that corresponds to (400) planes for the orthorhombic TiO_2/Cu_2O which is in accordance with the value of the interplanar distance d. The XRD pattern also reveals that the sample is polycrystalline in nature. The lattice parameters, a, and b for the orthorhombic structure is given as a = 5.4558Å, and b=14.29 Å. The average grain sizes for the samples are shown in table 1.

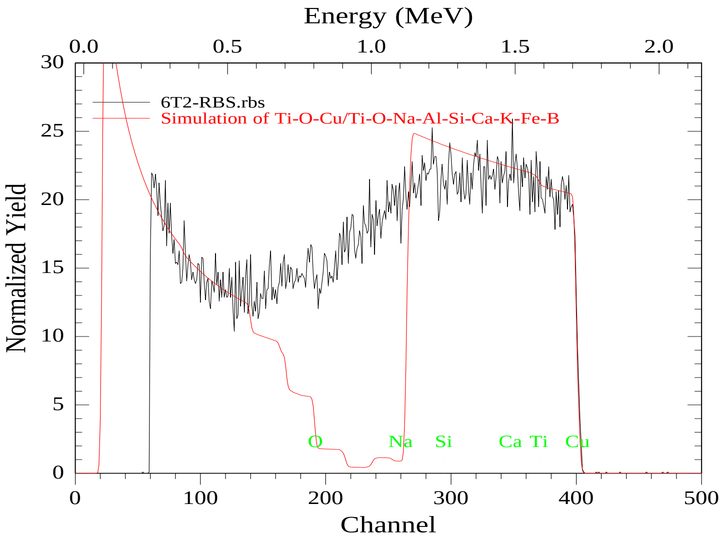

Fig. 1: RBS of TiO_2/Cu_2O

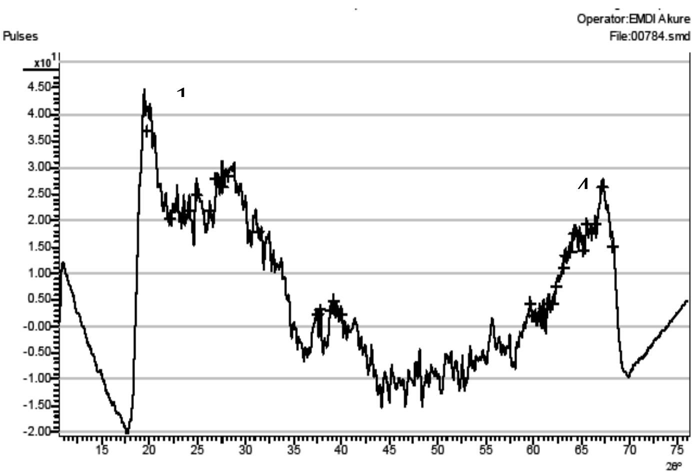

Fig.2a: XRD for as-deposited TiO_2/Cu_2O Thin Film

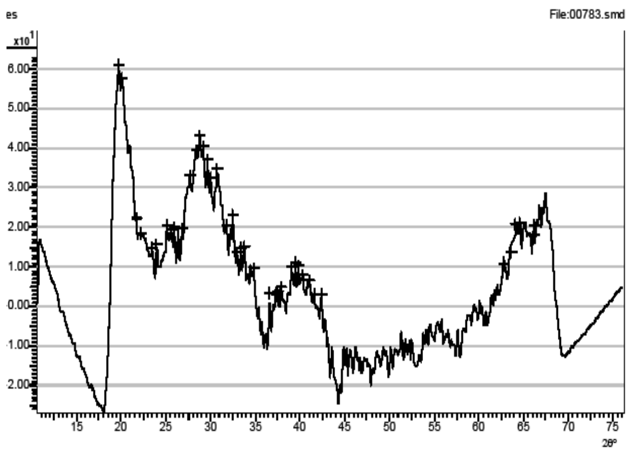

Fig.2b: XRD for $TiO_2/$ Cu_2O Thin Film Annealed at 373K

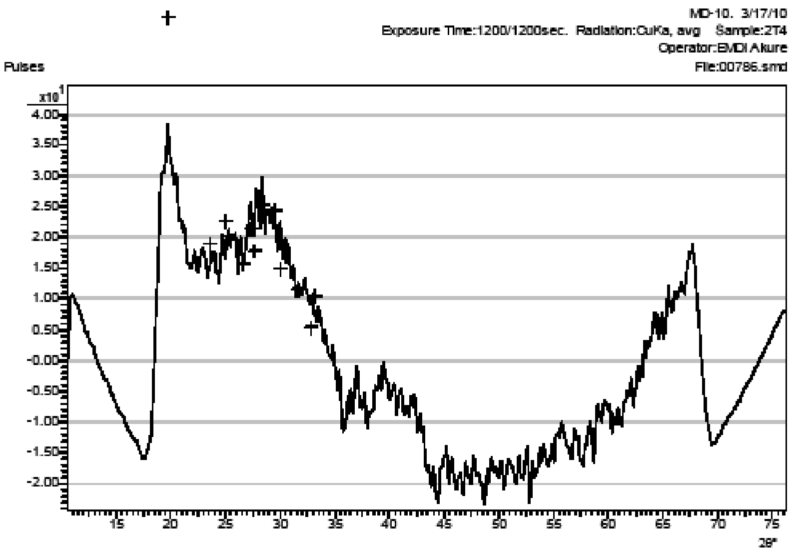

Fig.2c: XRD for $TiO_2/$ Cu_2O Thin Film Annealed at 673K

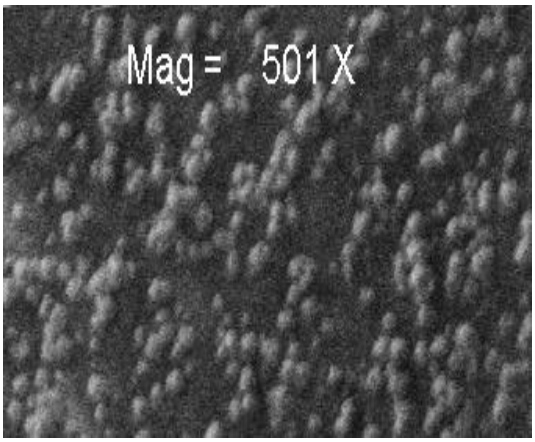

Fig.3a: SEM results for as-deposited $TiO_2/$ Cu_2O Thin Films

Figures 3a-c show the scanning electron Microscopy of the films under review The figure indicates that the aggregate grains increases with annealing temperature with small nano-sized particles engaged in a flower-like structure indicating the nanocrystalline nature of TiO_2/ Cu_2O thin films.

The spectral absorbance of TiO_2/ **Cu_2O** core/shell film is displayed in Figure 4. It is observed that absorbance decreased with increasing wavelength immediately after the fundamental absorption edge for all the samples. The film annealed at 673K has high absorbance in the visible portion of the solar spectrum. All the samples displayed low absorbance in the IR and FIR portion of the solar spectrum. However the sample annealed at 673K showed a better absorbance in IR and FIR when compared to other samples. The highest temperature annealed film transmits poorly in the IR and FIR portion of the solar spectrum. All the samples showed non-transmittance in the UV portion. It can also be thought that the absorbance and transmittances of the films were influenced by scattering due to irregular grains or aggregates. Such an explanation can be understood by the surface microstructure shown in fig.3a where the degree of irregularity in the grain size distribution were severe compared to other films. [10] TiO_2/ **Cu_2O** thin films could be used as spectrally selective window coatings in cold climate to facilitate transmission of visible (VIS) and NIR portion of the solar spectrum while suppressing the UV portion. TiO_2/MnO thin films can also be used for coating eye glasses for protection from sunburn caused by UV radiations.

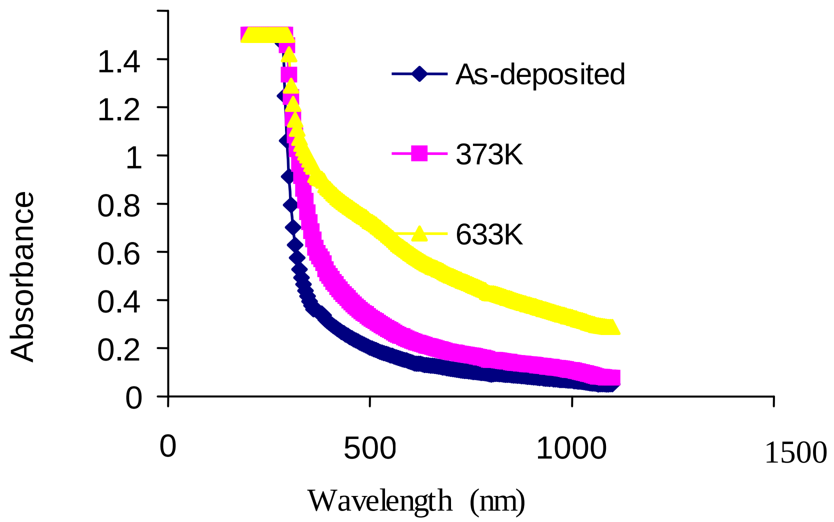

Fig. 4: Absorbance against wavelength for TiO_2/ **Cu_2O** thin Films

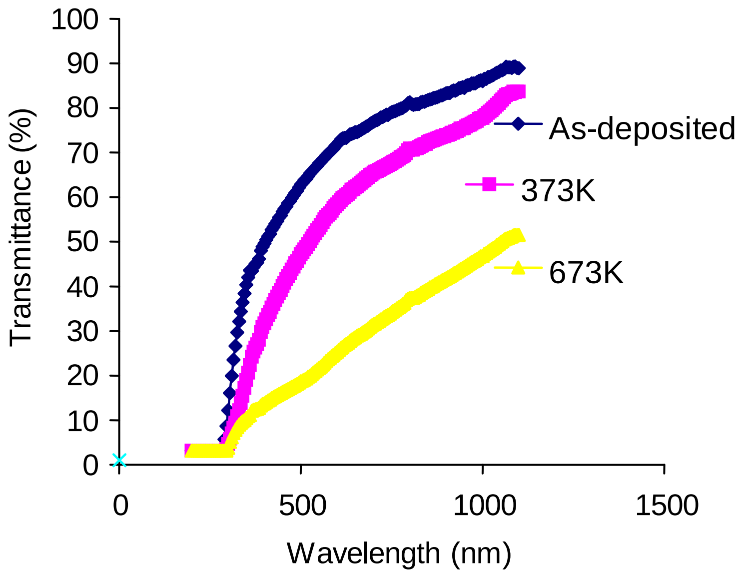

Fig. 5: Transmittance against wavelength for TiO_2/ Cu_2O thin Films

The variation of the refractive index, n for TiO_2/ Cu_2O is displayed in Fig.6. The index of refraction, n observed a peak around 2.45 and decreases with increasing wavelength at low energies. The minimum value of n is around 1.1 within the UV region. The film annealed at 673K has a maximum value of 2.2 within the UV range. For as-deposited and samples annealed at 373K and 673K, n increased, reached a peak and start to fall uniformly. The sample annealed at 673K displayed a different trend. Here n decreased from the maximum to almost zero with increasing photon energy. This behaviour suggests that these transparent films seem to behave like a transparent insulator. Transparent insulators are expected to prevent high UV while allowing only visible light. However this does not agree with the films grown. A transparent insulator in our case admits UV-Vis-NIR radiations hence it can be used as thermal control coatings. The annealing process has been noted to be helpful in improving the elect-optical properties of films. These enhancements have been attributed to a better crystalline quality and oxygen deficiency after the annealing. Transparent films like TiO_2/ Cu_2O are good candidate for optical filters, polarizer, narrow pass band etc.

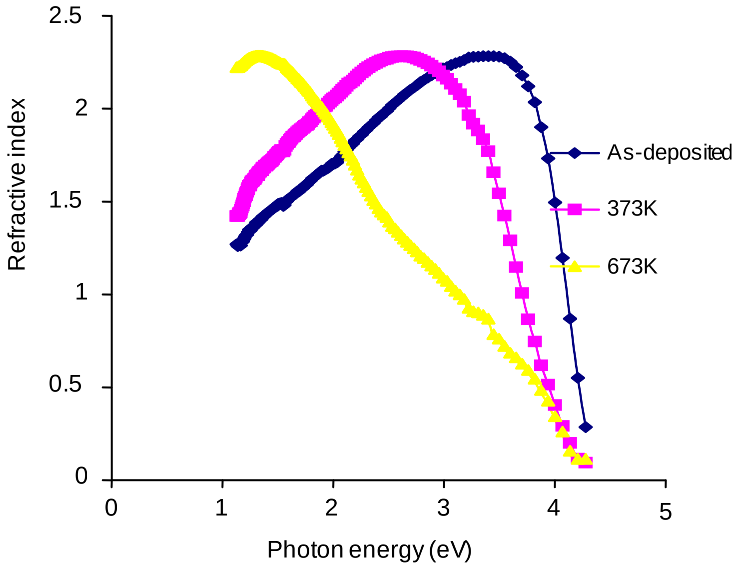

Fig.6: Variation of refractive index against photon energy for TiO_2/ Cu_2O thin Films

According to [11], a change in energy band gap is given by

$$\Delta E_g = \frac{\hbar^2 \upsilon^2}{2R^2}\left(\frac{1}{Me} + \frac{1}{Mh}\right) - \frac{(1.76e^2)}{ER} \quad (3)$$

where M_e, M_h are the effective masses of electrons in the conduction band and holes in the valence band respectively and E is the static dielectric constant of the material ΔE_g is the change in the band gap. The first term represents the particle in a-box quantum localization energy and has an inverse square relation $\frac{1}{R^2}$ dependence where R is the particle radius, while the second term represents the Coulomb energy with $\frac{1}{R}$ dependence. Therefore as R increases due to the increase in the crystalline size associated with temperature annealing the value of ΔE_g will decrease. [8]

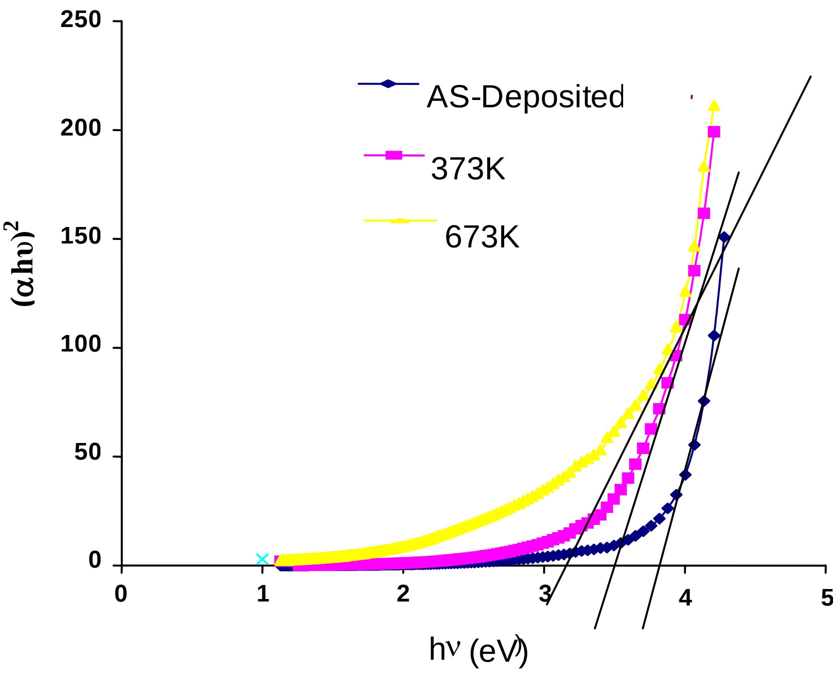

Fig. 7: $(\alpha h\upsilon)^2$ against photon energy for TiO_2/ Cu_2O Thin Film

From Fig.7, the values of the band gap are 3.89eV for as- deposited film, 3.52eV for sample annealed at 373K, 3.21eV for sample annealed at for 673K for TiO_2/ Cu_2O core/shell thin film. These suggest that high temperature annealing lowers the band gap of TiO_2/ Cu_2O although not too significant. The behaviour can be attributed to an increase in the carrier concentration (Moss-Burstein effect) [12] due to the presence of

Cu and its electrical activation probably improved by the annealing process, which decreases the potential barriers between grains. The large band gap possessed by this thin film implies that the film can be used for applications where electrical isolation is required such as cooling blankets for nuclear reactors.

4. Conclusion

In summary, this communication has demonstrated the possibility of depositing core/shell oxide thin film unto a glass substrate using the chemical bath technique.

XRD study reveals better crystallization of the films and band gap analysis show that high temperature annealing has pronounced effect on these properties. Calculated film thickness at various annealing temperature showed temperature dependence. The formation of T-iO_2/Cu_2O heterojunction considerably modified the optical properties and band gap of the independent film.

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