Effect of Uniform Decoration of Ag_2S Nanoparticles on Physical Properties of Granular TiO_2 Thin Films Synthesized by Using Spin Coating Technique

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In this work, we report the effect of uniform decoration of silver sulphide (Ag_2S) nanoparticles on physical properties of titanium dioxide (TiO_2) nanocrystalline thin films synthesized by using a spin coating technique by preparing TiO_2 gel using P-25 TiO_2, ethanol, acetyl acetone and p-hydroxybenzoic acid. Chemical bath deposited layer of Ag_2S particles enhance the properties of TiO_2 nanocrystalline thin films. The optical study reveals that the absorption edge shifts towards the visible region compared with the pure TiO_2 thin film due to the incorporation of Ag_2S nanoparticles into TiO_2 nanocrystalline thin films.

Keywords: Spin coating, Silver sulphide, Titanium dioxide, Nanocomposite, Optical properties.

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1. INTRODUCTION

Titanium dioxide (TiO_2) thin films have been studied substantially because of their wide range of applications, including photoanodes in photoelectrochemical (PEC) cells for the photocatalytic and photovoltaic purposes [1-3], gas sensing [4], protective material for transparent-conducting oxides used in silicon solar cell [5], optical filters and [6], antireflection coatings [7] etc. TiO_2 is inexpensive, non-toxic, chemically stable over a wide range of pH and electrically stable over a wide range of voltage [6, 8] and also it is biologically and chemically inert [9]. Although it possesses unique properties, TiO_2 is a wide band gap semiconducting material. So researchers have paid more attention to enhance the electrical conductivity of TiO_2 so as to increase the photoactivity of TiO_2 in the visible range [9]. In this context various materials like dyes and metallic nanoparticles have been used to improve the optoelectronic properties of TiO_2. In addition to these, metal chalcogenide semiconductors with narrow band gap which can absorb visible light, such as CdS, CdSe and PbS have been used as a sensitizers [10]. Compared with organometallic or pure organic dyes, semiconductors show greater stability; adjustable band gap which can tailor optical absorption over a wider wavelength range, and the possibility of exploiting multiple exciton generation to obtain high efficiencies [10, 11]. In this regard, we herein used solution-based method namely chemical bath deposition (CBD) to prepare Ag_2S that will be decorated on TiO_2 thin film prepared by sol-gel spin coating technique.

2. EXPERIMENTAL DETAILS

2.1 Substrate Cleaning

A glass microslide (of the dimensions 75 mm × 25 mm × 2 mm) is used as substrate. Prior to deposition, glass substrates were washed with double distilled water (DDW), boiled in chromic acid for 2 h. Again, the substrates were washed with detergent, rinsed in acetone and finally ultrasonically cleaned with double distilled water before deposition of thin film.

2.2 Chemical Deposition of TiO_2 Thin Film

TiO_2 thin films were prepared using sol-gel spin coating technique onto glass substrates. For this P-25 TiO_2 (Degussa, Germany) used as a precursor, ethanol and acetyl acetone as a solvent and *p*-hydroxybenzoic acid is used as a catalyst. The TiO_2 film was deposited by using spin coating technique by preparing TiO_2 gel. This gel was prepared by mixing 2gm of P-25 (Degussa P-25) with 8.5ml ethanol, 1.5 ml acetyl acetone and 1gm of p-hydroxybenzoic acid. The obtained mixture was continuously stirred for 8 hours at room temperature and then probe sonicated with the frequency of 20 KHz for 30 min. Now, 1 ml of prepared TiO_2 gel was dropped one time onto the centre of glass substrate. The substrate was accelerated with the different r.p.m. with different time and finally a uniform film was obtained. The synthesized films were annealed under oxygen at 400 °C for 45 minute which results the formation of porous TiO_2 thin film.

2.3 Chemical Bath Deposition (CBD) of Ag_2S Thin Film

Room temperature deposition of nanocrystalline Ag_2S thin film films by using the CBD technique in a

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silver nitrate-ammonia-thiourea system has been reported earlier [12]. The deposition process consists of: complexation of silver cations by ammonia and the consecutive reaction with the sulphide ions provided by hydrolysis of thiourea. The chemical bath contains aqueous solution of 20 ml of 0.1M silver nitrate and 20 ml of 0.6M thiourea. Aqueous ammonia was added into this solution to adjust the pH at the desired value (≈ 10). Then, mixture is stirred well. This reaction mixture was transferred into a beaker, in which the substrates were kept vertically. The deposition was carried out in a 100 ml beaker at a room temperature for 30 minute. Thereafter substrate coated with Ag_2S was removed, rinsed with distilled water, and dried in open air at room temperature for 15 minute. Film obtained was uniform, well adherent and blackish gray in color.

Chemical deposition of TiO_2/Ag_2S thin films.

In order to study the effect of uniform decoration of Ag_2S nanoparticles on physical properties of granular TiO_2, Ag_2S film was deposited onto TiO_2 thin films, which were previously deposited on glass substrate using same conditions as mentioned in section 2.3.

2.4 Characterization of Ag_2S, TiO_2, TiO_2/Ag_2S Thin Films

Characterization of all samples was carried out with different techniques. Structural properties were determined by X-ray diffraction technique by the means of an automated Bruker D8 advance X-ray diffractometer with CuKα radiations ($\lambda = 1.541$ Å) in 2θ ranging from 20° to 80°. S-4800 Type-II (HITACHI HIGH TECHNOLOGY CORPORATION Tokyo, Japan) field emission scanning electron microscope (FE-SEM) with an energy dispersive spectrometer (EDS) attachment was used for the determination of morphology and elemental chemical composition of the sample. To study the optical characteristics of the film, absorbance spectra were recorded in the range 370-900 nm by means of JASCO UV-VIS spectrophotometer (V-630). The resistivity of the CdSe thin films was determined by the standard two-probe method.

3. RESULTS AND DISCUSSION

3.1 Structural Analysis

Fig. 1 illustrates the XRD patterns of the prepared Ag_2S, TiO_2 and TiO_2/Ag_2S composite films. Fig. 1a illustrates the XRD patterns of the Ag_2S thin films obtained by chemical bath deposition technique onto glass substrate. The XRD pattern of the as-deposited Ag_2S films of thickness 348 nm shows a sharp diffraction peak at angular position $2\theta \approx 25.87^o$, 29.09^o, 31.63^o, 34.39^o, 36.73^o, 37.87^o, 40.72^o and 43.78^o to the prominent reflections, which found to be well indexed with the standard JCPDS data file 75-1061[13] and indicated monoclinic crystal structure. As evident in the Fig. 1b, XRD pattern of the TiO_2 thin films prepard by using spin coating technique on glass substrate shows single phase of TiO_2 tetragonal structure according to JCPDS card no. 84-1285. All diffraction peaks corresponding to (1 0 1), (0 0 4), (2 0 0), (2 1 1) and (2 0 4) planes were fully indexed and confirming the formation of nanocrystalline TiO_2 thin films anatase phase. The average crystallite size, determined from the well intense peaks for Ag_2S and TiO_2 films by using the Scherrer's semi-empirical formula were 27.52 and 20.45 nm, respectively.

After chemical bath deposition of Ag_2S onto TiO_2 thin films, the XRD pattern (Fig. 1c) of TiO_2/Ag_2S composite is very similar to the naked Ag_2S and TiO_2 films. The intense peaks appears at $2\theta \approx 29.09^o$, 31.63^o, 34.39^o and $2\theta \approx 25.31^o$ are charcteristics of Ag_2S and TiO_2, respectively. These peaks still present in the XRD pattern of TiO_2/Ag_2S composite, indicating the stability of the two compounds during the synthesis process [14]. This result confirms the TiO_2/Ag_2S composite was successfully prepared.

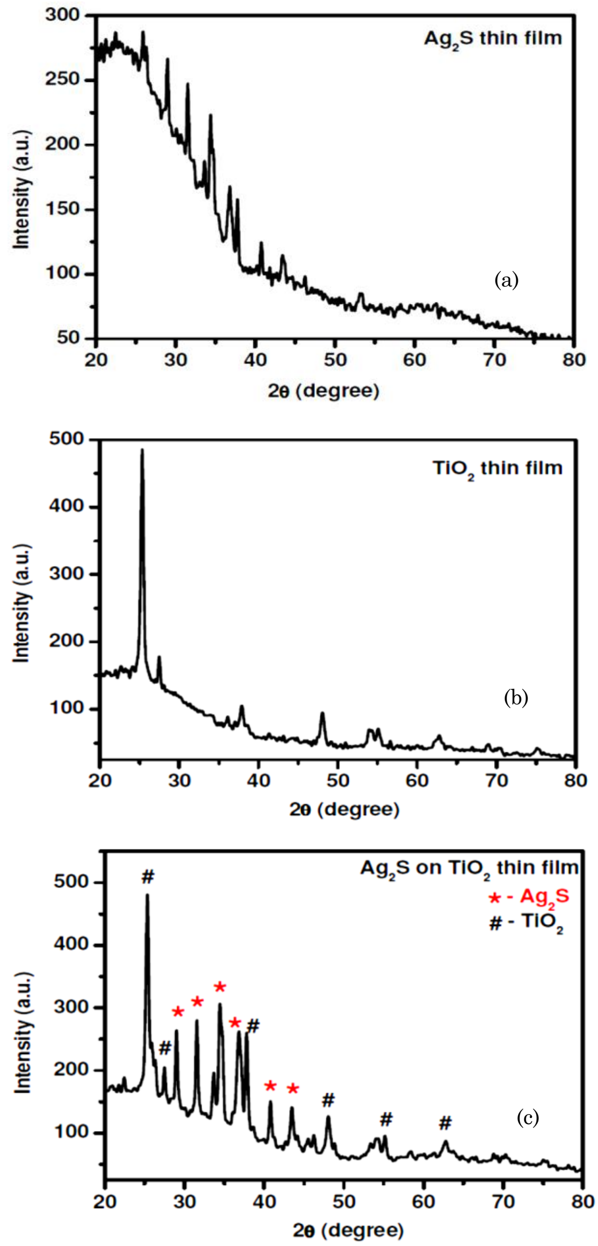

Fig. 1 – XRD pattern of (a) Ag_2S, (b) TiO_2 and (c) TiO_2/Ag_2S composite thin films

3.2 Surface Morphology and Compositional Studies

Fig. 2 (a) and (b) shows the FE-SEM images of Ag_2S, TiO_2 thin films obtained by chemical bath deposition and sol-gel spin coating technique, respectively prepared onto glass substrates. It can be observed that the surface of the obtained Ag_2S and TiO_2 thin films is homogeneous, smooth and cracks-free. Both the films are consisted of fine, uniform, densely packed nanoparticles which are in agreement with the XRD results.

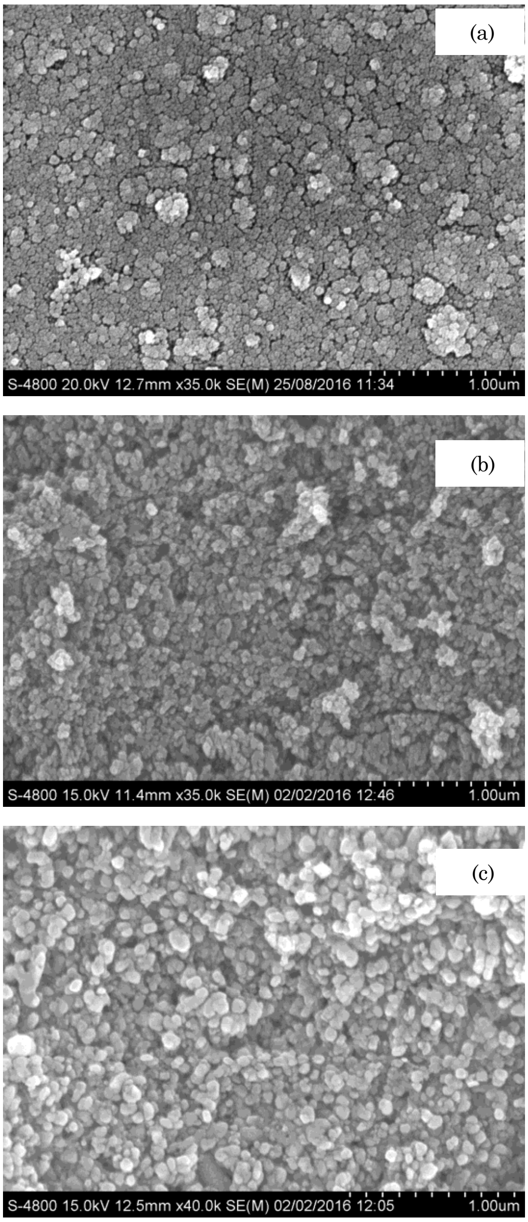

Fig. 2 – FESEM images of (a) Ag_2S, (b) TiO_2 and (c) TiO_2/Ag_2S composite thin films

The average grain size for Ag_2S thin films was slightly smaller than the TiO_2 grains. This difference in the grain size of the two thin films is attributed to different chemical kinetics (CBD and sol-gel spin coating) and preparative conditions [14]. Fig. 2c shows the FE-SEM image of Ag_2S decorated TiO_2 thin films. It may be noted here that the grains of Ag_2S deposited onto TiO_2 were spherical in nature but very much larger in size compare to pure TiO_2 (Fig. 2b). The morphology change confirms the formation of uniform TiO_2/Ag_2S composite thin films.

The typical EDS spectrum for TiO_2/Ag_2S composite thin films is shown in Fig. 3. It is observed that the emission lines of 'Ti', 'Ag' 'S' and 'O' are present in the EDS spectra indicating the formation of TiO_2/Ag_2S composite thin films.

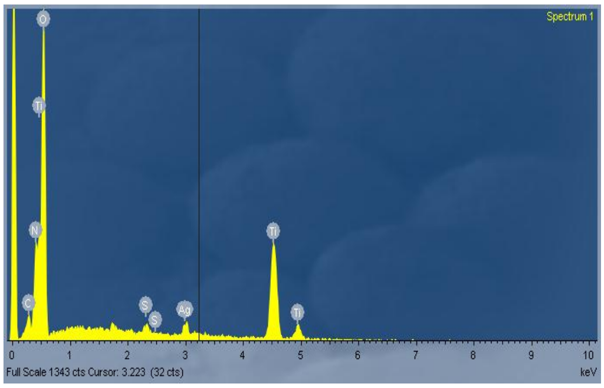

Fig. 3 – Typical EDS pattern of TiO_2/Ag_2S composite thin films

3.3 Optical Properties

The optical properties of Ag_2S, TiO_2 and TiO_2/Ag_2S composite films were characterized by UV-VIS absorption spectra as shown in Fig. 4.

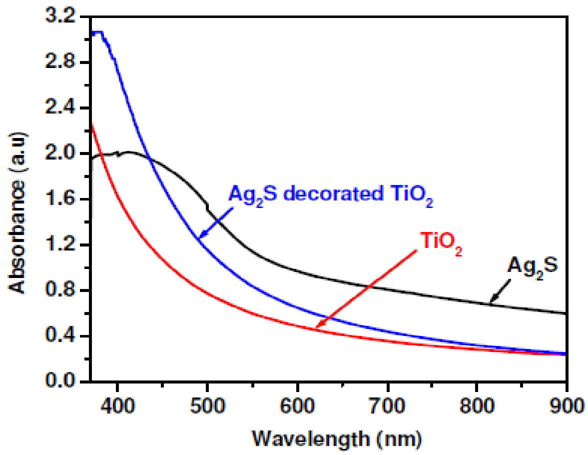

Fig. 4 – Absorbance with respect to wavelength for (a) Ag_2S, (b) TiO_2 and (c) TiO_2/Ag_2S composite thin films

The absorption spectra of TiO_2 thin films shows a strong absorption in the wavelength between 400 and 450 nm. Also from the Fig. 4 we can obsrved that the Ag_2S thin films have a broad absorption in the wavelength between 400 to 600 nm. From the fig. 4, it can be seen that the absorption edge shifts towards the visible region compared with the pure TiO_2 thin film due to the incorporation of Ag_2S nanoparticles into TiO_2 nanocrystalline thin films. It means that incorporation of Ag_2S nanoparticles into TiO_2 thin films caused red shift of absorption edge.

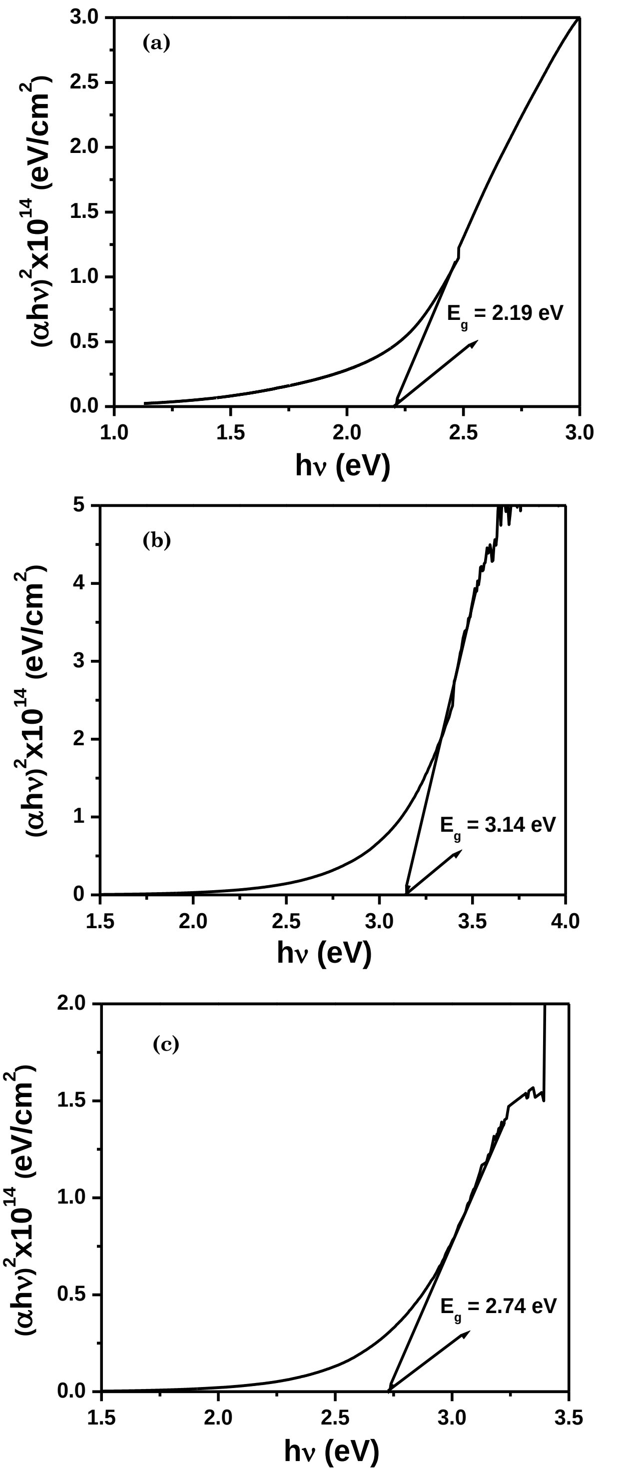

Fig. 5 – Plot of $(\alpha h\nu)^2$ versus $h\nu$ for (a) Ag_2S, (b) TiO_2 and (c) TiO_2/Ag_2S composite thin films

Therefore, TiO_2/Ag_2S composite films are expected to use in the light harvesting devices such as solar cells and photoelectrochemical cells [15]. The band gap of pure TiO_2 thin film was 3.14 eV, which is comparable to the band gap of TiO_2 thin films prepared on glazed porcelain substrates by using sol-gel process [16] and it is decreased to 2.74 eV after incorporation of Ag_2S nanoparticles onto TiO_2 thin films as shown in Fig. 5 (c).

3.4 Electrical Studies

Fig. 6 shows the plot of logarithmic resistivity versus the inverse of temperature for Ag_2S, TiO_2 and TiO_2/Ag_2S composite films. From the plot it is clear that, for all samples the resistivity decreases with increase in temperature indicating semiconducting behavior of these films [17]. The activation energy for TiO_2/Ag_2S composite films (0.1082 eV) lies in between that for Ag_2S thin film (0.3564 eV) and TiO_2 films (0.0867 eV), which indicates the improvement in the electrical properties of Ag_2S nanoparticles decorated granular TiO_2 thin films.

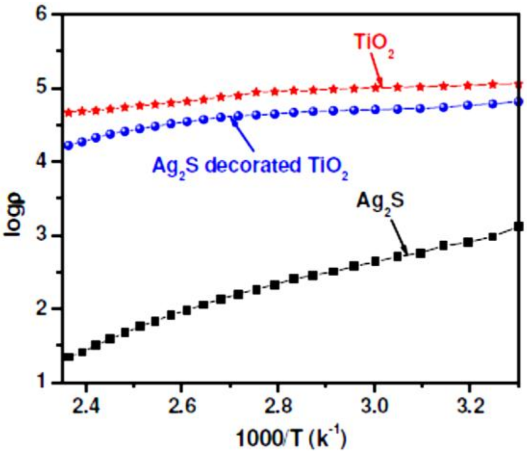

Fig. 6 – Plot of logarithmic resistivity versus the inverse of temperature for Ag_2S, TiO_2 and TiO_2/Ag_2S composite films

4. CONCLUSION

To summarize, we have reported on the effect of uniform decoration of Ag_2S nanoparticles on physical properties of granular TiO_2 thin films synthesized by using spin coating technique. It has been found that the morphological, optical and electrical properties of the TiO_2 thin films are modulated by the Ag_2S decoration on TiO_2 thin films.

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