INFLUENCE OF SILAR CYCLE ON STRUCTURAL AND OPTICAL PROPERTIES OF COPPER SULPHIDE (CuS) THIN FILMS FOR PHOTOVOLTAIC APPLICATION

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Abstract

The effect of variation of Successive Ionic Layer Adsorption and Reaction, (SIlAR) cycles was studied on the structural and optical properties of CuS thin films. The sources of copper and sulphur were copper nitrate and thiourea, respectively while soda lime glass served as the substrates. SILAR cycles were varied between 30 and 60. The film thickness was determined by a double weight method. The thicknesses of the films were 69 nm, 86 nm, 122 nm and 143 nm at 30, 40, 50 and 60 cycles, respectively. The XRD measurements showed that the films were polycrystalline in nature and the transmittance was between 75 and 82.8 % and the band gap energy varied between 2.05 and 2.40 eV as revealed by UV visible spectrophotometer measurement. The films are suitable for transmission of solar radiation into absorber layer of a thin film solar cell. Therefore, it is recommended to replace cadmium sulphide (CdS) which is popularly used as a window layer in the fabrication of thin film solar cell.

Keywords: band gap, cycle, polycrystalline and transmittance.

Introduction

Solar energy technology is among the most attractive alternative sources of energy. It has the advantages of non-limited, non-polluted and easy to use over other alternative energy sources. The amount of energy produced by sun in a year is more than 10,000 times the world 's yearly energy needs. Thus, solar energy is proposed to be the hope to human's future.(Mitwallyová, 2014; Rowley & Westwood, 2003). To be able to make use of this energy, it requires a converter or transducer which converts it for the desired needs. Photovoltaic (PV) devices convert sunlight into electrical energy, and they are commonly known as solar cells. The PV devices separate light induced carriers (electrons and holes), and extract them generating electricity (Fluieraru et al., 2019). Semiconductors are the basic materials in fabricating solar cells. The first-generation solar cells were made from silicon materials with high efficiency. The recent reported photoelectric conversion efficiency (PCE) for crystalline Si cell is 25% (Pujotomo& Aita Diantari, 2018) However, they have some disadvantage such as high cost of manufacturing process because the SiO needs to be of high purity and low absorption of high energy photons due to thick layers of the absorbing material is required. Hence, thin film solar cells are brought to overcome the challenges of Si solar cell (Kibria et al., 2014)

Thin film solar cells are introduced as the second generation of solar cells, to provide high production capacity at lower energy and material consumption. The growth of thin film PV are motivated due to their potential for high-speed, high-throughput manufacturing and minimum material requirements that lead to cost reduction. They are made on cheap, large area and non-silicon substrates such as glass, metal foil or plastic.

Thin film solar cells were divided into three main subcategories due to their absorber materials; amorphous silicon (a-Si), cadmium telluride (CdTe) and copper-indium-gallium-diselenide (CIGS). These materials are direct-gap semiconductors that absorb incoming solar radiation at a thickness much thinner than the required thickness of silicon wafers in crystalline silicon (Si) solar cells. Thin film solar cells are either homojunction, heterojunction or multi-junction devices, and are formed from combination of metallic elements from group I, II and III and nonmetallic element from group V, VI and VII in the periodic table. The examples are numerous and not limited to binary compound semiconductor such as CuS, ZnTe, ZnS, ZnSe (Chowdhury et al., 2017; Osanyinlusi, 2020), ternary compound such as CIS, InGaAs, and quaternary compounds such as $CuInGaSe_2$,Cu_2ZnSnS_4(Jiang, 2011: Asokan & Velauthapillai, 2014) The thin film solar cells are made of two dissimilar materials to form heterojunction which consists of an absorber layer and window layer. The window layer transmits maximum amount of light to the absorber layer which absorbs the radiation and convert it to electricity. The window layer is deposited on top of the

absorber layer (Acevedo-Luna *et al*., 2017; Mukhopadhyay *et al*., 2019; Ong *et al*., 2018). This layer should have minimal absorption loss, low surface recombination and electrical resistance in photogenerated carriers, protect the junction against chemical reactions and mechanical damage. Also, the layer should optimize band alignment of the cell and make a wide depletion region with p-type absorber layer. This minimizes the carriers tunneling and maintain higher open circuit voltage value which later establish a higher contact potential. The transparent part (window layer) of the structure can be either constructed with or supplemented with conducting oxides. Those can be fabricated into a photovoltaic device. Ultimately, the device needs to be optimized for the amount of light absorption necessary for the power generation and the transparency necessary for structural functionality (Bin Rafiq *et al*., 2020).

Among binary semiconductors, copper sulphide (CuS) is one of the most researched semiconductor in class of group II-VI because it has wide applications in areas of photo electrolysis, photocatalysis, and photoelectrochemical power generation (Sangamesha et al., 2013), flat-panel displays, light emitting diodes, defrosting windows, and other optoelectronics (Al-khayatt, 2013). Copper sulphide (CuS) forms five stable phases: (i) Covellite (ii) anilite (iii) digenite (iv) djurtite and (v) chalcocite at room temperature (Arcthu & Ikasa, 2019).

Different methods have been employed by several researchers to synthesis CuS thin film, the methods include thermal evaporation (Sahoet al., 2015), electrsoless plating (Arcthu & Ikasa, 2019), chemical bath deposition (Orori et al., 2014; Osuwa & Mgbaja, 2014), Successive Ionic Layer Adsorption and Reaction (SILAR) method (Mitkari et al., 2019; Taşdemirci, 2019). The SILAR method is employed for this study due to its simplicity, economical and suitability for any substrates.

2 Materials and Methods

1.208 g of copper nitrate and 3.808 g of thiourea were separately dissolved in 100 ml distilled water to make 0.1 M of copper solution and 0.5 M sulphur solution respectively. Soda lime glasses were used as substrates. They were soaked in aqua regia solution for 24 hrs, washed with detergent, rinsed with distilled water and they oven-dried for 15 min at 40^{o}C.

The SILAR method involves four steps. In the first step, the glass substrate was dipped into a beaker which contained the copper solution for 30 s and then rinsed in the second beaker that had distilled water for 20 s. The glass was then dipped into sulphur solution for 30 s in the third beaker to grow sulphur ions and lastly rinsed with distilled water in the fourth beaker for 20 s. This process completed a cycle. For this study 30,40, 50 and 60 cycles were made to grow CuS films onto glass substrates, the films were annealed in an oven (Gen Lab) at 200^{o}C for 1 hr. The thicknesses of the films were determined by double weight method according to Eqn (1)

Thickness (t) of the films = $\frac{change\ in\ the\ mass\ of\ substrate}{Area\ of\ the\ substrate X\ theoretical\ density\ of\ CuS}$ **(1)**

The crystal structures of the films were examined by X-ray diffractometer (Rigaku D/Max-lll developed by the Rigaku Int. Corp. Tokyo). The source of X– ray radiation was Cukα radiation, the scanning angle varied in the range 2-60^{o} with a wavelength of 1.5405 Å. The optical transmittance of the films was measured with AVANTEX UV visible spectrophotometer in the wavelength range of 239.534 nm to 999.495nm.

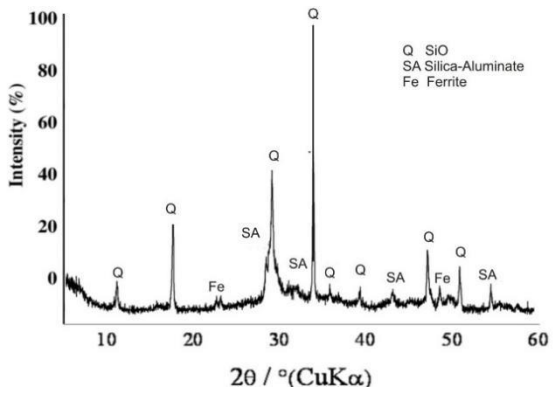
3 Results and Discussion

Structural Properties

Fig.(1a-d) show structural patterns for CuS thin films at different SILAR cycles. The figures show the intensity of the peak against $2\theta$for the thin films using *Cuk*αradiation source with wavelength of 1.5405 Å.The figures reveal the nature of the films as polycrystalline structure. A similar structure has been reported by Sahoo et al. (2015). The pattern reveals every material present in the films such as SiO, silica- aluminate, ferrite and zeolite. SiO is the most prevalent and intense material. The soda lime glass substrate that served as the mechanical support of the film could be a factor for this. The patterns of the films at 30, 40, and 50 cycles are similar. However, the pattern of films at 60 cycles revealed the presence of zeolite. The higher value of film thickness of 143 nm could be a factor for the deviation (Usoh et al., 2014) . The interplanar spacing'd'of the most intense peak was determined according to Bragg's in Eqn (2)

$$n\lambda = 2dsin\theta \quad (2)$$

Table 1 shows the interplanar distance with corresponding angle for different SILAR cycles. It can be seen that as the SILAR cycle increased, the interplanar spacing increased. The increase in film thickness could be a factor for this increment



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Fig.1a: XRD pattern for CuS thin film for 30 cycles

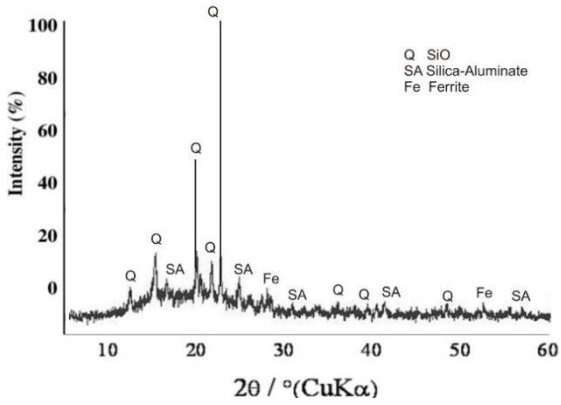


Fig. 1b : X-ray diffraction pattern for 40 cycles

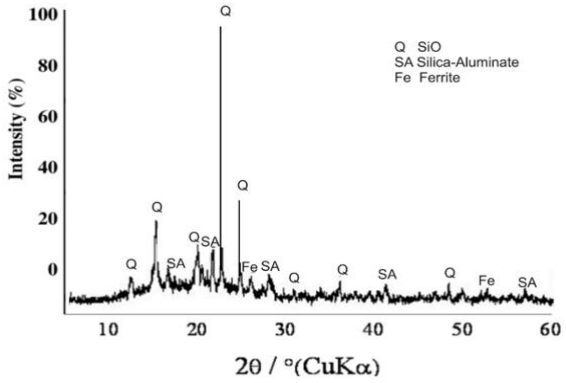


Fig.1c.: X-ray diffraction pattern for 50 cycles

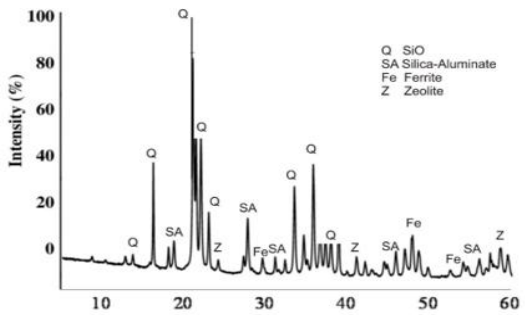


Fig.1d.: X-ray diffraction pattern for 60 cycles

Table 1: The SILAR cycles and interplanar spacing

Cycles	Θ/degree	d/Å
30	17.0	6.39
40	12.0	7.45
50	11.5	7.75
60	11.0	8.11

Optical Properties

Fig. 2 and 3 are transmittance spectral and band-gap energy, respectively at different SILAR cycles. The transmittance increases in the visible region (Fig. 2). The maximum transmittance was between 75 and 82.8 %. The film deposited at 30 SILAR cycles exhibited the maximum transmittance while the films at 60 SILAR cycle showed

the minimum transmittance. The increase in the film thickness as cycle increased may be a factor for this. The absorbance (A) of the films was calculated according to Eqn (3). The absorbance coefficient (α) was determined using Eqn (4). The photon energy was calculated according to Eqn (5). The Tauc's relation in Eqn (6) was used to determine the optical band gap energy from the Fig. 3.

$$A = 2 - logT\% \quad (3)$$

$$\alpha = 2.303A/t \quad (4)$$

$$E = 1243/\lambda \quad (5)$$

$$\alpha hv^2 = A(hv - Eg) \quad (6)$$

The extrapolated band gap energies are 2.40, 2.30, 2.10 and 2.05 eV for films at 30, 40, 50 and 60 cycles, respectively. The energy decreased as SILAR cycle increased. The increase in film thickness from 69 nm to 143 nm could be a factor for variation of the band gap energy. The result is within the range of 2.0 – 2.53 eV obtained by Aethur & Ikasa (2014), Mitkari et al. (2019) and Usoh et al. (2014).

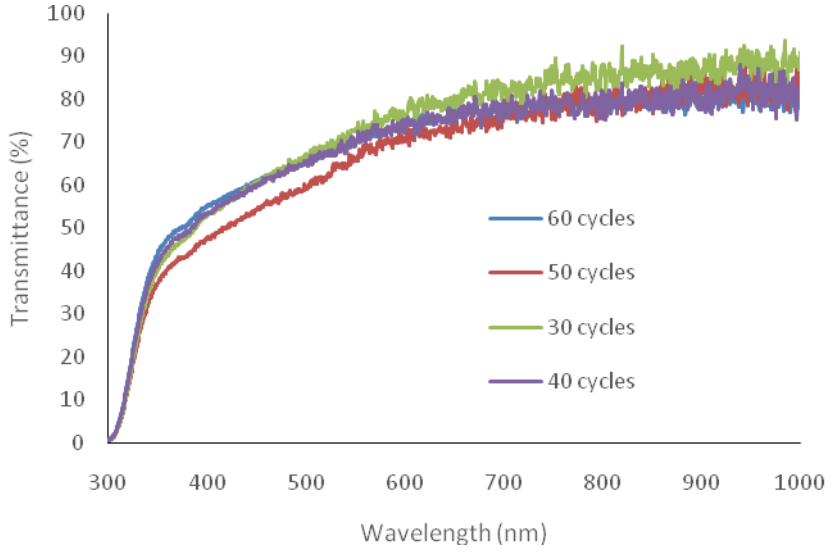


Fig.2: Transmittance spectral at different SILAR cycles

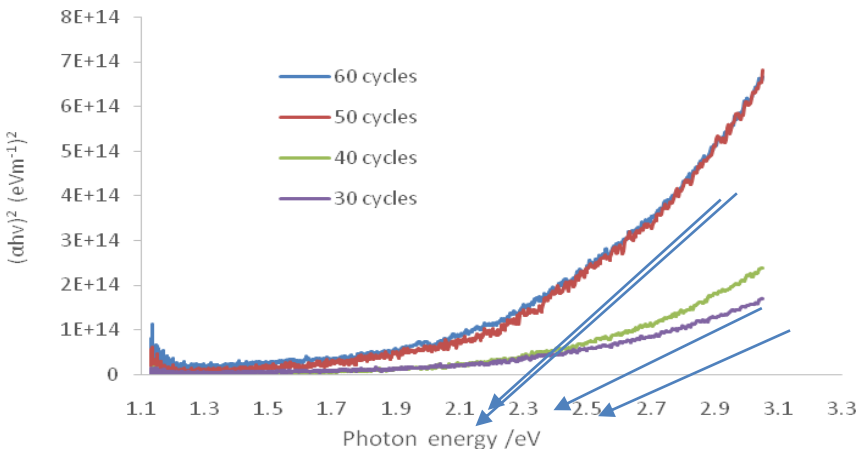


Fig.3: Band gap energy at different SILAR cycles

Conclusion

Successive Ionic Layer Adsorption and Reaction (SILAR) method was employed in deposition of CuS thin films onto soda lime glass substrate. The influence of variation of SILAR cycle on the structural and optical properties of the films was studied. The films exhibited polycrystalline properties and high transmittance when examined by X-ray diffractometer and UV visible spectrophotometer. The results showed that lower thickness of film led to high transmittance and high band gap energy in the visible region. The films of CuS thin film that deposited at 30 and 40 cycles can be used as a buffer layer in fabrication of thin film solar cell to replace toxic CdS.

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