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# Prospects and challenges of silver sulphide thin films: A review

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### ABSTRACT

Silver sulphide (Ag<sub>2</sub>S) has been a subject of investigation over the years for possible applications in various optoelectronics, electronics and industrial applications. Materials cost, abundance of the constituents elements, and its efficiency in use are fundamental properties in selecting materials for use as absorber or window layers in solar cell devices, or other optoelectronic applications. This paper reviews recent published work on the subject of Ag<sub>2</sub>Sbased solar cells and nano applications. The reasons for the sudden interest in the utilisation of  $Ag_2S$  by the scientific community for  $Ag_2S$  solar cells and other applications are discussed; coupled with the crystallographic and optoelectronic properties, including  $Ag_2S$  crystalline structure, defect formation and metal composition. This review paper focuses on  $Ag_2S$  synthesis processes and device properties.

Keywords: Silver sulphide, optoelectronic, solar cell devices, efficiency, synthesis

## INTRODUCTION

The sustainability of photovoltaics (PV) production requires that research in the PV industry must be geared toward the development of a new PV technology based on abundant and more environmentally acceptable elements. Photovoltaics has been generally accepted as one of the most promising options to produce renewable and green electricity, with thin film PV a major stakeholder in cost reduction potentials. The use of silver sulphide thin films for applications in various electronics, optoelectronics, and in the coating industry has been established over the years. Silver sulphide belongs to the chalcogenide group (Ag belongs to I-VI compound semiconductor materials with monoclinic crystal structure). The basic requirements for a material to be utilised as an absorber or window layer for a heterojunction solar cell device are many and varied because of the dependence of material properties on other parameters that ranges from atomic to bulk scale. For example, the optical response of most optoelectronic devices depends specifically on the optical properties of the constituent materials and this will in turn, give an insight on how effectively and efficiently these devices can utilise photons depending on the applications. It has been established [1] that the efficiency of a solar cell amongst other factors is a function of how many photons the window layer can transmit to the absorber layer, the number of photons the absorber layer is capable of absorbing and effectively converting into electron-hole pairs, and the nature of the contacts. Another important fundamental factor for consideration in enhancing the efficiency of solar cells is the nature of the conductivity of the absorber layer and the density of defects in the layers/and or junction. P-type absorber layers are mostly preferred in thin film solar devices because the minority carrier diffusion length of electrons in a p-type semiconductor is much larger than that of the holes in a n-type semiconductor. Presence of defects can adversely affect the absorption and transport properties of the materials since they are potential recombination sites/traps, leading to a reduction in the device performance. Silver sulphide has been successfully utilised in solar cells as window/buffer layers due to its

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excellent opto-electronic properties [2-3], coatings [4-5], sensors [6-10], atomic switches, photo-switches, and resistive switches [11-15], infrared photography [16], thermoelectrical cells [17-18], optical imaging [19], electronic devices [12-13, 20-22], solar cells [23-27], photocatalytic applications [28-31], infrared detectors [32], photoconductors [33-34], electrochemical storage cells [35], laser recording media [36], and sensitizers [37-38]. Research work by [23], indicate that Ag<sub>2</sub>S based-solar cells with solar conversion efficiency > 1.5% can be achieved. Several research groups have reported on the photoelectric and thermoelectric properties of silver sulphide thin films [39-43]. In the literature, considerable efforts on the synthesis and characterisation of silver sulphide to explore their potential applications have been reported, thus Ag<sub>2</sub>S thin films can be grown using different low-cost but efficient deposition techniques such as: spray pyrolysis [44-46], SILAR- successive ionic layer reaction and adsorption [23, 47-51], photodeposition [52], thermal evaporation [53-56], microwave irradiation assisted methods [57], solvothermal routes [58-59], chemical bath deposition [2-3, 48, 60-74], hydrothermal synthesis [75-76], solution growth technique [77-80], hard template method [81], template free method [82], chemical synthesis [5, 57, 83-111] electrodeposition [82, 112-126], sonochemical method [127-129], epitaxial method [130-132], gamma irradiation [133], aerosol assisted chemical vapour deposition [134-135], sulphurisation method [136-137], pair cell method [138], chemical vapour deposition [139-140], and reverse micro emulsion method [141].

Although several scholars have reported on the low abundance and high cost of silver, the use of silver to enhance efficiency in different optoelectronic applications and in the nanotechnology industries is very common. It has been established that the efficiency of some optoelectronic devices can be greatly enhanced through silver additives especially in quantum dot solar cells as sensitizers [142-143]. Some research group [8], opined that amongst all other noble metals, the best localized surface plasmon resonance response are mostly obtained from silver nanoparticles, thus making it potential candidate for various optoelectronic applications. The amphoteric nature of the thin films of  $Ag_2S$  have been established in the literature. It has been reported that silver sulphide thin films exhibit a p-conductivity type [55, 77], and n-conductivity type [3, 50, 68-69, 79, 107, 124, 144-145]. This makes it more adaptable to different device designs.

In the literature, review work on silver sulphide is very rare hence to the best of our knowledge, this is the first review report on silver sulphide related devices and there is no doubt that this study will form a comprehensive and fundamental basis for further research in application and utilisation of silver sulphide related applications.

#### MATERIALS AND METHODS

This research work was carried out using a literature based conceptual approach, thus the author comprehensively reviewed the literature of silver sulphide thin films independent of the deposition techniques. The study investigates the limitations of silver sulphides in application of some optoelectronic devices with special emphasis on crystallographic properties, defects formation and material synthesis.

#### **RESULTS AND DISCUSSION**

Silver sulphide (Ag<sub>2</sub>S) is an important chalcogenide compound which has been investigated for its numerous applications and widely believed to belong to the group of the I–VI compound semiconductor materials with monoclinic crystal structure. The three major crystal structure are; monoclinic or acanthite ( $\alpha$ -form), body centered cubic or argentite ( $\beta$ -form), and a high temperature face-centered cubic ( $\gamma$ -form). Using chemical bath deposited Ag<sub>2</sub>S thin films, some authors [146] obtained single phase layers that crystallized in the acanthite crystal structure. Reports [125, 138, 147-149], indicate that the stability of silver sulfide depends on temperature hence it occurs as mixed ionic and electronic conductor above 200 °C while the stable temperature regime of the three allotropic forms are:  $\alpha$  (monoclinic phase stable up to 142 °C),  $\beta$  (bcc phase stable from 142 °C to 600 °C), and  $\gamma$  (fcc phase stable above 600 °C). Other research groups [35, 150-151], also reports that the three allotropic forms are stable at different temperature ranges:  $\alpha$ -Ag<sub>2</sub>S (monoclinic, stable up to 178 °C),  $\beta$ -Ag<sub>2</sub>S (bcc, 178 °C - 600 °C), and  $\gamma$ -Ag<sub>2</sub>S (fcc, > 600 °C). However different research groups [74], and [152], noted that silver sulphide presents two main allotropic crystallographic modifications: monoclinic acanthite ( $\alpha$ -Ag<sub>2</sub>S) and cubic modification argentite ( $\beta$ -Ag<sub>2</sub>S). The ionic nature of silver sulphide thin films was also reported by other research groups [54]. Research work by Sharma and Chang [152], further observed that the argentite form exhibits quasi-metallic behavior, a factor that makes it less favourable for semiconductor applications.

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In the literature [153], it has been noted that a reproducible sample preparation techniques that will yield thin films of desired stoichiometry is critical in the study of the conductance and switching properties of Ag<sub>2</sub>S thin films. Silver sulphide thin films have been established to exhibit p-type and n-type conductivity independent of the deposition technique. However it is yet not clearly stated on the possible reasons responsible for the variation. For instance, it has been reported that the kësterite structure allows for several types of point defects which make discrete energy levels appear, allowing p-type doping in kësterite thin films while for certain chalcopyrites (CIGS copper indium gallium diselenides), it is influenced by stoichiometric variations [154]. The ionic nature of Ag<sub>2</sub>S films have been earlier mentioned. Other authors [155], identified Schottky and Frenkel defects as the two major types of point defects that occurs in ionic crystals. Defects such as interstitials and vacancies in ionic solids, move by hopping transport mechanism instead of band-like transport phenomena. It is generally known that Frenkel defects are formed by the displacement of either the anion or cation from the lattice site to an interstitial site, and mostly occurs as Frenkel defects (displacement of a cation to the interstitial site) or Anti-Frenkel defects (displacement of an anion to the interstitial site) [156]. Research done by [22], indicates that the cationic Frenkel defect formation is commonly found in silver halides and chalcogenides. The report of Smyth [155] earlier attributed this to the fact that silver cation has the unique property of not acting like a rigid sphere and this allows it to deform and move through interstitial sites in a crystal. Further, charge recombination has been cited as the cause of the low efficiency of quantum dot solar cells [25]. Although some scholars [22] argue that these point defects enhances wider utilization of silver sulphides in industrial applications such as in film photography, fuel cells, and as catalytic agents, defects are known to be detrimental to the efficiency of solar cell devices.

The intrinsic property of a material is one of the most important and fundamental criterion for selection of such material for use in device applications. These include; energy bandgap, optical absorption coefficient, electron and hole mobility, minority carrier diffusion length, refractive index, electrical conductivity and carrier concentrations among others. Reports in the literature of silver sulphide thin films exhibits some degree of discrepancy in some of these properties as indicated in Table 1. Table 1 show that the nature of the optical transition in silver sulphide films are either direct or indirect transitions. The energy band gap obtained from experimental data is reported to be within the range of 0.8 eV to 2.3 eV, implying that silver sulphide films can be used as absorber or window layers in solar cell devices, optical filters, infra-red dectors, etc. The energy band gap values are mostly derived from absorbance measurement. However, some authors [157], worked on the ab-initio calculation of Ag<sub>2</sub>S and reported an energy bandgap of 0.06 eV. Research work by [158], indicated that absorbance measurements are not suitable for extracting the bandgap values since the absorption coefficient derived from spectrophotometric data on thin films is determined by defect absorption and by measurement accuracy limitations amongst other factors. The optical absorption coefficient is reported to be of the range  $10^4$  cm<sup>-1</sup> to  $10^5$  cm<sup>-1</sup> [46, 144], implying that thin layers can be used as absorber layers (as photons are absorbed close to the junction interface) in solar cell devices. However the solar conversion efficiency of silver sulphide based solar cells is still very low (< 3%). The photovoltaic parameters of silver sulphide based devices as contained in current literature reports are summarised in Table 2. The low solar conversion efficiency could be attributed to the wide discrepancy in the calculated theoretical energy bandgap value with those from the experimental reports as observed in this study. The donor density of silver sulphide is reported to be  $5.63 \times 10^{16}$  cm<sup>-3</sup> [124], effective carrier mobility of 5 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> - 10 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> [74], carrier lifetime of 0.1 µs [64], room temperature conductivity in the order of  $10^{-3}$  ( $\Omega$  cm)<sup>-1</sup> [74, 144] and the electrical resistivity in the range  $10^4$  ohm-cm –  $10^5$  ohm-cm [68].

The conventional superstrate or substrate configuration mostly used in thin film solar cell devices are less reported in the literature for silver sulphide based solar cell devices. Most silver sulphide based solar cells are common as quantum dot solar cells with few variations in the architecture. However the solar conversion efficiency is still very low in both cases as shown in Table 2. Chen and co-workers [25], reported that an inclusion of a ZnO recombination barrier layer between TiO<sub>2</sub> nanotubes and Ag<sub>2</sub>S quantum dots, reduced the charge recombination in Ag<sub>2</sub>S quantum dot sensitized solar cells and hence increased the conversion efficiency of the Ag<sub>2</sub>S-sensitized TiO<sub>2</sub> nanotubes. Jadhav et al. [2], reported a very low efficiency of 0.002 % in their investigations and attributed it to the presence of interface states, nanocrystalline grain size of Ag<sub>2</sub>S films and high series resistance of the films. In the literature, various scholars have reported that large grain size are known to be among the critical factors that determines high efficiency in thin film solar cells independent of the deposition techniques [154, 156, 163].

No.	Energy bandgap	Refractive index	Nature of Transition	Ref.
1	0.9 eV - 1.05 eV		Direct	[74]
2	2.2 eV		Not given	[77]
3	1.1 eV		Direct	[55]
4	1.0 eV		Direct	[64]
5	1.56 eV	2.52	Direct	[71]
6	1.78 eV - 2.09 eV		Direct	[63]
7	1.95 eV			[110]
8	1.05 eV		Direct	[134]
9	2.09 eV		Direct	[3]
10	1.85 eV		Indirect	[124]
11	2.17 eV – 2.09 eV		Direct	[47]
12	1.33 eV		Direct	[135]
13	0.06 eV			[157]
14	1.3 eV		Direct	[159]
15	2.3 eV		Indirect	[159]
16	1.76 eV		Direct	[111]
17	1.71 eV		Indirect	[160]
18	1.14 eV	2.38-2.81	Direct	[46]
19	0.96 eV		Indirect	[54]
20	1.2 eV		Direct	[126]
21	1.07 eV	1.44-3.18	Direct	[144]
22	1.1 eV-1.4 eV	0.91-2.2	Direct	[72]
23	0.8-0.9 eV			[161]
24	1.15 eV		Direct	[162]
25	0.91 eV		Indirect	[162]

Table 1: Some Optical Constants of Silver Sulphide

The film thickness of silver sulphide thin films according to current reports [46, 62, 68, 78, 117, 145, 164] are mostly in the order of few microns or nanoscale. It has been established that the absorber layer thickness should be large enough to provide substantial grain size which must be several times the average optical absorption length for solar photons in order to reduce the loss of photogenerated carriers [1, 165-167]. Further, the absorber layer thickness must be large enough to absorb most of the incident radiation and to support the contact voltage. Large grain sizes generally lead to reduced grain boundaries (reduced density of short circuit paths) to increase the solar conversion efficiency of solar cell devices.

XPS studies by Krylova [153] and Hota et al., [168] did not give a clear account on the heterojunction band alignments but the former only confirmed a formation of silver sulfide on the polypropylene surface with a sheet resistance in the range 39  $M\Omega/cm^2$  to 3.5  $M\Omega/cm^2$ .

No.	Isc (mA/cm <sup>2</sup> )	FF	Voc (V)	η (%)	$Rs(\Omega)$	$Rsh(\Omega)$	Ref.
1	0.080	0.085	0.325	0.002	291	709	[2]
2		0.27		1.1			[124]
3				0.28			[25]
4	1.54			1.70			[23]
5	13.7			0.49			[169]

Table 2: Photovoltaic parameters of Ag<sub>2</sub>S-based solar cells

#### CONCLUSION

The major aim of this is review is to create a platform to identify the fundamental steps that will enhance increased efficiency in  $Ag_2S$  based solar cells and in other optoelectronic, electronics, and in solar thermal applications; through identification of the major setbacks limiting the efficiency of  $Ag_2S$  based-devices as reported in the literature. The low solar conversion efficiency based on the current literature report is attributed to; the wide difference between the theoretical value and the experimental value of the energy bandgap, and the low value of the absorber layer thickness and small grain sizes. Moreso, the energy bandgap is reported to be indirect [54, 124, 159-160, 162, 170] while some research groups also show direct energy bandgap as summarised in Table 1. In quantum-dot solar cells, the efficiency of quantum dot silver sulphide based-solar cells are mostly limited by charge recombination amongst other factors. However successful use of  $Ag_2S$  nanoparticles in different applications is common in the literature, and this strongly suggest that though silver sulphide is not possibly a good absorber layer

for applications in photovoltaic solar cell devices in lieu of the small crystallites/grain sizes, it is quite beneficial in other applications.

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