Nanostructured copper sulphide films deposited from a precursor bath prepared using RO water

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Abstract

Synthesis of functional nanostructured materials using solution-based low-cost deposition routes is an emerging research area. In this paper, we report deposition of one such material, Copper Sulphide nanostructures (CuS NS), using low-cost chemical bath deposition technique. The films have been deposited on bare glass substrate from a precursor (PS) bath prepared using reverse osmosis (RO) processed water (Drinking water). The deposition of the films has been carried out at three different temperatures, 60°, 65° and 70 °C. X-ray diffraction study confirmed the CuS NS film possess pure hexagonal covellite phase. Scanning Electron Microscopy of the films revealed the flower-like shape CuS NS are made up of hexagonal plates of side lengths ∼38 nm and thickness ∼4.76 nm. The average size of the agglomerated grains was calculated 65 nm to 665 nm (60 °C), 94 nm to 670 nm (65 °C) and 94 nm to 670 nm (70 °C) using ImageJ software. The optical study showed the films possess indirect and direct optical energy bandgap (Eg) in the range ∼1.3–1.6 eV and ∼2.4–2.7 eV, respectively.

1. Introduction

Nanostructured materials prepared using low-cost solution-based deposition routes have potential to exploit low-purity, earth-abundant elements. The need of the hour is to develop simplest deposition techniques to synthesize functional nanostructures. Transition metal chalcogenide copper sulphide, CuS, is a p-type semiconductor having a wide range of optical energy bandgaps [1]. It belongs to a class of solar photovoltaic (SPV) materials which are synthesized by using low-grade non-toxic elements. It is one of the materials prominent to form extensive variety of stable non-/stoichiometric and mixed phases such as, covellite (CuS), anilite (Cu1.75S), digenite (Cu1.96S), djurleite (Cu1.97S) and chalcocite (Cu2S) at R.T. Nanostructures of CuS are profusely used in various applications ranging from SPV [2, 3] to energy storage devices [4–6], and gas sensors [7–9] to superconductivity [10]. The stable phase, covellite CuS, has been deposited by various solution-based film deposition techniques such as, chemical bath deposition (CBD) [11, 12], microwave-assisted CBD (MACBD) [13], electrodeposition [6, 14], mechanochemical [15], etc. Here, we report deposition of pure phase CuS NS films from aqueous chemical bath prepared using RO-drinking water at RT.

2. Experimental

Copper sulphide films were deposited in one-step using Chemical Bath Deposition (CBD) technique. The typical deposition procedure requires precursor solution (PS) prepared using copper chloride dihydrate (CuCl2·2H2O) (0.3M), sodium thiosulphate (Na2S2O3) (1M), N-N' dimethyl thiourea (0.5M) and RO water. This PS bath (pH: 6.0) containing vertical glass substrate was then introduced into the bath. Deposition of the films was carried out at 60°, 65° and 70 °C temperature for 4h. After deposition, the substrates were removed...
from the bath, washed with RO water and dried at 60 °C. The chemicals used were of Analytical grade supplied by Merck Ltd., Mumbai, India.

The structural study of CuS NS films was carried out by x-ray diffraction (XRD) plots (θ/2θ) recorded with a Bruker, D2 Phaser x-ray Diffractometer (with CuKα radiation) in the range 10° to 70°. Morphology study of the films was done with the Scanning Electron Microscope (SEM, Jeol, JSM6010LA). The transmittance spectra of NS CuS films were measured using UV–vis–NIR spectrophotometer (Shimadzu, UV–3600) in the wavelength range 200–2500 nm.

2.1. Deposition of CuS NS films
The chemical bath deposition of CuS NS films can be explained as follows: at first precursor solution (PS) was prepared by taking 5 ml aqueous solution of copper chloride dihydrate (CuCl2.2H2O) into a beaker, to which 9 ml aqueous sodium thiosulphate (Na2S2O3), a complexing agent, was added drop-wise. This mixture was then stirred vigorously for 2–3 min. In the beginning, precipitates were formed which dissolved later on addition of more Na2S2O3. It was added till the solution became clear. At this stage, CuCl2 in water produces a complex Cu(II) hexahydrate aqua ion, [Cu(H2O)6]2+ as depicted by Reaction (1).

\[ \text{Cu}^{2+} + 6\text{H}_2\text{O} \rightarrow [\text{Cu(H}_2\text{O)}]_{6}^{2+} \] (1)

Further, addition of sodium thiosulphate to the PS produces thiosulphate \( S_2O_3^{2-} \) and hydrogen sulphide ions. These ions present in the solution gradually replaces the \( \text{H}_2\text{O} \) molecules and produces ionic thiosulphatocopper(I) complexes, \( [\text{Cu(S}_2\text{O}_3)_n]^{2n-1+} \) [16].

\[ [\text{Cu(H}_2\text{O)}]_{6}^{2+} + n\text{S}_2\text{O}_3^{2-} \rightarrow [\text{Cu(S}_2\text{O}_3)_n]^{(2n-1)+} \] (2)

\[ \text{S}_2\text{O}_3^{2-} + \text{H}_2\text{O} \rightarrow \text{SO}_3^{2-} + \text{HS}^- + \text{H}^+ \] (3)

The complex, \( [\text{Cu(S}_2\text{O}_3)_n]^{(2n-1)+} \), further dissociates into \( \text{Cu}^+ \) and \( S_2O_3^{2-} \) ions.

\[ [\text{Cu(S}_2\text{O}_3)_n]^{(2n-1)+} \rightarrow \text{Cu}^+ + n\text{S}_2\text{O}_3^{2-} \] (4)

These \( \text{Cu}^+ \) ions are unstable in the presence of air and undergo disproportionation reaction to form metallic \( \text{Cu}(\text{Cu}^0) \) state and \( \text{Cu}^{2+} \) ions.

\[ 2\text{Cu}^{2+} \rightarrow \text{Cu}^{2+} + \text{Cu}^0 \] (5)

Simultaneously, dimethyl thiourea, a sulphur source, was added drop-wise (10 ml) to the constantly stirring precursor solution. This reaction releases the hydrosulphide ions \( \text{HS}^- \), as given by Reaction (6) and (7).

\[ \text{CH}_3\text{NHCSNHCH}_3 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{NHCONHCH}_3 + \text{H}_2\text{S} \] (6)

\[ \text{H}_2\text{S} + \text{H}_2\text{O} \rightarrow \text{HS}^- + \text{H}_3\text{O}^+ \] (7)

Finally, the released ions, \( \text{Cu}^{2+} \) and \( \text{HS}^- \), form nanostructured CuS films by condensing on the surface of the glass substrate.

\[ \text{Cu}^{2+} + \text{HS}^- \rightarrow \text{CuS} + \text{H}^+ \] (8)

3. Results and discussion
Semi-transparent and adhesive CuS NS films were deposited on glass substrates at temperatures 60°, 65° and 70 °C. However, there was no film formation at 55 °C and below, while temperature higher than 70 °C yielded non-uniform, non-adhesive patchy deposits. The films get peeled off due to terminal thickness at temperatures higher than 70 °C. The X-ray diffractogram of CuS NS films deposited on glass substrate at different temperature is shown in figure 1. All the diffraction peaks have been identified and indexed to the hexagonal phase CuS (JCPDS: 6-464). As revealed in diffractogram, (002) line is dominantly very sharp and strong with weak (100) line. The increased peak intensity at 65 °C temperature confirms the CuS films are more crystalline than those deposited at 60° and 70 °C. Close observation leads to twinned peaks which may be due to the diffraction from the twinned planes or to transmission diffraction [17]. All the diffraction peaks show shift in peak position with respect to standard data which is attributed to the uniform strain on the films. The relative intensity of diffraction lines did not increase for deposition temperature 70 °C. This may be attributed to the fact that at higher deposition temperatures, the higher thermal energy only accelerates the rate of chemical reaction, with no remarkable improvement in the relative intensity of peaks.

Figure 2 represents scanning electron microphotographs of CuS NS films deposited on glass substrate at different temperatures. The films consist of nanostructured flowers made-up of hexagonal plates. As shown in figure 2(a), irregular shaped grains with some triangular and hexagonal shapes are deposited on the substrate. The cross-section (inset image) reveals the films are dense and non-uniform having thickness ~100–200 nm.
The average grain size distribution, as shown in the histogram, ranges from 65 nm to 665 nm. This range includes agglomerated grains too. At higher temperature, 65 °C (figures 2(b), (c)), the nucleation density increases, and mixed growth of rods, flakes and irregular-shaped grains of CuS NS is observed throughout the film. Some of these rods/flakes are twinned, some are partially grown and some are well-grown. This process can be divided into three stages: growth of bare rods/flakes, intermediate growth of grains from the rods/flakes and growth of well-developed grains. The isolated grains are hexagonal plates (marked with red colour hexagonal ring). At higher magnification (figure 2(c)), the microphotograph reveals formation of flower-like nanostructures with hexagonal sheets stacked one-over-other. The film is dense and possesses thickness of 500 nm. The average grain size of these nanostructures, as calculated from ImageJ software, varies in the range 94 nm to 670 nm. In general, it is observed the agglomeration of extensively distributed grains (figure 2(c)) formed from randomly oriented flakes/rods as shown in figure 2(b). Figure 2(d) shows microphotograph of CuS film.
Nanostructured hexagonal plates of side lengths ~38 nm and thickness ~4.76 nm and side length ~38 nm. These plates form cross-linked structures at an obtuse angle 130° or an acute angle 50°. The growth process has completed at 70 °C and no intermediated growth of grains observed, which are present at 65 °C (figure 2(b)). No remarkable change in the size of the nanostructures is observed at this temperature. All these structures show the degree of randomness of aligned nanostructures decreases as the temperature increases, and hence, uniform growth of grains is observed. The average size of agglomerated grains, as calculated from ImageJ software, was determined as 275.28 nm. Thickness dependent optical properties of CuS NS thin films were investigated in the wavelength range 200–2500 nm as shown in figure 3. The transmittance spectra of the films show about 56% transmittance at around 550 nm in the visible region of the spectral range. The absorbance of the films increases as the wavelength decreases from 500 nm. Badshah et al [11] have reported the CuS nanostructures absorb in the visible region from 400 to 500 nm with a strong blue emission band at 465 nm making it a good photoluminescent material with potential applications in light emitting devices and biological labelling. Other chalcogenide material, ZnS, has also revealed interesting optical properties for application as antireflection coatings [18], buffer layer in solar cells [19] and photo catalysts [20]. As shown in figure 3, the absorbance of the films increases with the deposition temperature. The thickness of the films increases resulting in lower transmittance. The indirect and direct optical bandgap (Eg) of CuS NS films was calculated from Tauc relation, \( (\alpha h\nu)^{1/n} = A(h\nu-E_g) \), where, \( \alpha \) is absorption coefficient, \( h\nu \) is photon energy, \( A \) is constant and exponent \( n \) depends on the type of transition (\( n = 1/2, 2 \) for indirect/direct allowed transitions). Extrapolation of linear portion of the curve \( (\alpha h\nu)^{1/n} \) versus \( h\nu \) gives the indirect and direct bandgap values. These values vary with the temperature as shown in figures 4(a) and (b). As depicted in figure 4(a), the films possess indirect bandgap ~1.6 eV for 60 °C and 65 °C deposited films and 1.3 eV for 70 °C deposited films. Since the growth of nanostructures saturates at 65 °C, no remarkable change in the values of direct bandgap are observed at higher temperature. As temperature increases, bandgap decreases due to increased grain size. Thickness dependent optical properties of CuS NS thin films have been reported by Faris et al [21]. As the thickness of the film increases, the number of collisions of incident photons with the atoms on the surface of the films increases, which results in the increased value of the absorbance. The values of direct bandgap of the films, as shown in figure 4(b), varies with the deposition temperature: 2.7 eV (60 °C), 2.3 eV (65 °C) and 2.4 eV (70 °C). Since the growth of nanostructures saturates at 65 °C, no remarkable change in the values of direct bandgap are observed at higher temperature. Such different values of band gaps has been reported for different morphologies of CuS NS [1]. These values are 2.08 eV for CuS microspheres, 2.06 eV for CuS nanotubes, 2.16 eV for CuS nanoflakes and 1.88 eV for CuS nanoparticles providing different absorbance edges in UV and visible regions.

4. Conclusions

Semi-transparent, adhesive CuS NS films have been deposited from a precursor bath prepared from RO-drinking water at RT. Nanostructured films belong to covellite hexagonal crystal system. The film consists of nanostructured hexagonal plates of side lengths ~38 nm and thickness ~4.76 nm. The films are continuous and well covered with grain size ranging from 65 nm to 670 nm. Optical energy bandgap values of the film suggest CuS NS films can be used as potential absorber material for the low-cost solar cell.
Acknowledgments

The authors are grateful to the Chairman and Provost of Charotar University of Science and Technology for funding this work and allowing them to publish.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Conflict of interests

Authors of this research article declare no conflict of interest.

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References

[1] Shamraiz U, Azadar R and Badshah A 2016 Fabrication and application of Copper Sulphide (CuS) nanostructure J. Solid State Chem. 238 25–40
[2] Nair P K, Nair M T S, Fernandez A and Ocampo M 1989 Prospects of chemically deposited metal chalcogenide thin films for solar control applications J. Phys. D: Appl. Phys. 22 829–36
[3] Isac L, Duta A, Kriza A, Manolache S and Nana M 2007 Copper sulfides obtained by spray pyrolysis- Possible absorbers in solid-state solar cells Thin Solid Films 515 5755–8
[4] Rui X, Tan H and Yan Q 2014 Nanostructured metal sulphides for energy storage Nanoscale 6 9889–925
[5] Chen X, Huang Y, Zhang K and Zhang W 2017 Cobalt fibers anchored with tin disulphide nanosheets as high-performance anode materials for lithium ion batteries J. Colloid Interface Sci. 506 291–9
[6] Kadam S L, Bulakhe R N, Kadam R A and Yewale M A 2020 Electrochemical synthesis of CuS Thin film for supercapacitor application Macromol. Symp. 392 1900209 1-5
[7] Huynh T-P 2020 Chemical and biological sensing with nanocomposites prepared from nanostructured copper sulphides Nano Futures 4 032001 1-27
[8] Sabah F A, Ahmed N M, Hassan Z and Rasheed H S 2016 High performance CuS p-type thin film as a hydrogen gas sensor Sens. Actuators A Phys. 249 68–76
[9] Tian X, Qian L, Mao J and Yuan H 2013 In Situ synthesis of CuS nanotubes on Cu electrode for sensitive nonenzymatic Glucose sensor Sens. Actuators B Chem. 176 932–9
[10] Tezuka K, Sheets W C, Kurhara R, Shan Y J, Imoto H, Marks T J and Poeppelmeier K R 2007 Synthesis of covellite (CuS) from the elements Solid State Sci. 9 95–9
[11] Chaki S H, Deshpande M P and Tailor J P 2014 Characterization of CuS nanocrystalline thin films synthesized by chemical bath deposition and dip coating techniques Thin Solid Films 550 291–7
[12] Mohammed K A, Ahmed S M and Mohammed R Y 2020 Investigation of structure, optical, and electrical properties of CuS thin films by CBD technique Crystals 10 684
[13] Xin M, Li K and Wang H 2009 Synthesis of CuS thin films by microwave assisted chemical bath deposition Appl. Surf. Sci. 256 1436–42
[14] Chen Y, Davoise C, Tarascon J-M and Guéry C 2012 Growth of single-crystal copper sulfide thin films via electrodeposition in ionic liquid media for lithium ion batteries J. Mater. Chem. 22 5295–9
[15] Achimovičová M, Tóthová E, Daneu N, Dutková E, Zubrík A and Fabián M 2020 Simple preparation and properties of surface modified mecanochemically synthesised copper sulphide semiconductor Mater. Sci. Technol. 36 1257–62
[16] Diliegros Godinesa C J, Lombardero-Juareza D I, Machorro-Mejaic R, Silva González R and Pal M 2019 Electrical properties and spectroscopic ellipsometry studies of covellite CuS thin films deposited from non ammonical chemical bath Optical Mater. 91 147–54
[17] Goswami A 1996 ‘Thin Films Fundamentals’ New age international
[18] Agbo P E, Nwofe P A and Odo L O 2017 Analysis on energy bandgap of Zinc Sulphide (ZnS) thin films grown by solution growth technique Chalcogenide Lett. 14 357–63 https://chalcogen.ro/357_AgboPE.pdf
[19] Nwofe P A, Robert B J and Agbo P E 2018 Influence of processing parameters on the structural and optical properties of chemically deposited Zinc Sulphide thin films Mater. Res. Exp. 5 106405 1-16
[20] Faris R A and Dahir M K 2016 Synthesis characterization and optical properties of nanostructured zinc sulfide thin films obtained by spray pyrolysis deposition Iraq J. Laser 15 9–12 https://ijl.uobaghdad.edu.iq/index.php/IJL/article/view/50 (Accessed: 7 January 2021)
[21] Yahya A M, Mahdi Z F, Faris R A and Mohammed G H 2014 Effect of the thickness on the optical properties of nanostructure CuS thin films Chem. Mater. Res. 6 47–54 https://www.iiste.org/Journals/index.php/CMR/article/view/10856/11160