



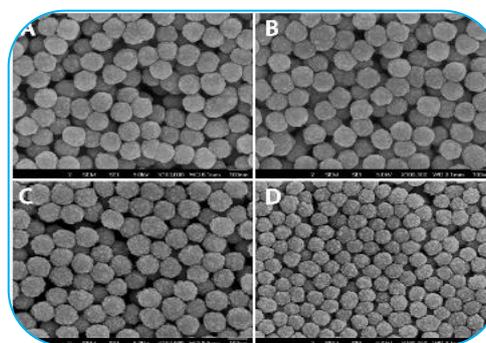
FACILE SYNTHESIS AND DETAILED CHARACTERIZATION OF Ag₂S NANOPARTICLES FOR ENHANCED OPTICAL AND RAMAN APPLICATION

Anuja Bhimrao Abdule

Department of Physics / Mahatma Phule Mahavidyalaya, Pimpri, Pune.

ABSTRACT

Silver sulfide (Ag₂S) nanoparticles and thin films were synthesized using the spin-SILAR method and investigated for surface-enhanced Raman scattering (SERS) applications. Optical properties were studied using UV-Vis-NIR spectroscopy, while surface morphology was analyzed by scanning electron microscopy (SEM). Energy-dispersive spectroscopy (EDS) verified the stoichiometric presence of Ag and S elements. Optical absorption analysis indicated strong visible-near infrared. The combined analyses confirm the successful synthesis of phase-pure Ag₂S nanoparticles suitable for optoelectronic and sensing applications. SERS measurements using Rhodamine 6G (10⁻⁴ M) under 532 nm excitation showed moderate enhancement attributed primarily to charge-transfer-mediated chemical enhancement. The results demonstrate that Ag₂S nanostructures function as semiconductor-based SERS substrates.



KEYWORDS : Ag₂S nanoparticles; Spin-SILAR; Semiconductor SERS; Charge transfer; Thin films.

1. INTRODUCTION

Silver sulfide (Ag₂S) is an important I-VI chalcogenide semiconductor that has attracted considerable attention due to its unique electrical, optical, and catalytic properties.^{1,3} It exists predominantly in the monoclinic acanthite phase at room temperature and exhibits a narrow direct band gap (~0.9–1.1 eV), making it highly suitable for near-infrared (NIR) optoelectronic applications.⁴ Unlike metallic silver, Ag₂S demonstrates excellent chemical stability, relatively low toxicity compared to other heavy metal chalcogenides, and strong absorption in the visible-NIR region, broadening its technological relevance.⁵

Nanostructured Ag₂S has emerged as a promising material for applications in photodetectors, biosensors, solar cells, photocatalysis, lithium-ion batteries, and surface-enhanced Raman scattering (SERS).^{6,9} At the nanoscale, Ag₂S exhibits size-dependent quantum confinement effects that significantly influence its band structure, optical absorption, and charge transport properties.¹⁰ Therefore, controlled synthesis and systematic characterization of Ag₂S nanoparticles are essential to tailor their physicochemical properties.

Various synthetic approaches have been reported for the preparation of Ag₂S nanostructures, including chemical precipitation, hydrothermal methods, solvothermal techniques, SILAR processes, and green synthesis routes.^{11,13} Among these, solution-based chemical synthesis offers advantages such as simplicity, scalability, cost-effectiveness, and better control over particle size and morphology.

However, phase purity, crystallinity, and stoichiometry strongly depend on reaction parameters. Hence, comprehensive structural and spectroscopic evaluation becomes crucial. Raman spectroscopy serves as a sensitive probe for lattice vibrations and Ag–S bonding characteristics.¹⁴ Energy-dispersive spectroscopy (EDS) confirms elemental composition and stoichiometric balance. Optical characterization further reveals semiconductor behavior and band gap properties, typically estimated via Tauc analysis.¹⁵ Despite extensive studies on Ag₂S nanomaterials, achieving phase-pure, stoichiometric nanoparticles with controlled crystallinity remains challenging. In this work, Ag₂S nanoparticles were synthesized via a controlled chemical route and comprehensively characterized using, Raman spectroscopy, EDS, and UV–Visible spectroscopy to establish structure–property relationships.

2. EXPERIMENTAL SECTION

Deposition of Ag₂S Thin Films via Spin-Assisted SILAR Technique

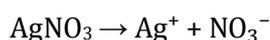
Ag₂S thin films were deposited using a spin-assisted successive ionic layer adsorption and reaction (spin-SILAR) technique employing a non-aqueous solvent system. The SILAR method is widely recognized as a cost-effective and controllable thin-film deposition approach for chalcogenide semiconductors.^{16,18} The selection of ethanol as the solvent was motivated by its relatively low surface tension and appropriate volatility, which facilitate improved wetting behavior, uniform precursor spreading, and controlled solvent evaporation during spin coating.^{19,20} These parameters are crucial for achieving homogeneous film growth while minimizing surface defects such as pinholes and agglomeration.

Silver nitrate (AgNO₃) and sodium sulfide (Na₂S) (Sigma-Aldrich, analytical grade) were used without further purification. Separate ethanolic precursor solutions of AgNO₃ (0.01 M) and Na₂S (0.005 M) were prepared under ambient conditions.

The spin-SILAR deposition cycle consisted of sequential ionic adsorption and surface reaction steps:

Step 1: Cationic Precursor Deposition

A precisely measured aliquot (50 μL) of 0.01 M ethanolic AgNO₃ solution was dispensed onto the pre-cleaned substrate. In solution, AgNO₃ dissociates as:



Step 2: Spin-Induced Adsorption

The substrate was accelerated to a predetermined rotational speed and maintained for a fixed duration. During spinning, Ag⁺ ions undergo electrostatic adsorption onto the substrate surface. The centrifugal force ensures uniform thinning of the precursor layer while removing excess solvent, thereby promoting formation of a surface-confined cationic layer.²¹

Step 3: Anionic Precursor Introduction

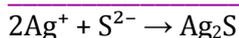
Subsequently, 50 μL of 0.005 M ethanolic Na₂S solution was introduced onto the rotating substrate. The sulfide precursor dissociates as:



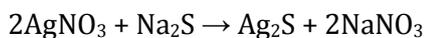
The S²⁻ ions diffuse toward and react with the adsorbed Ag⁺ layer.

Step 4: Interfacial Reaction and Film Formation

A heterogeneous surface reaction occurs between Ag⁺ and S²⁻ ions, resulting in the nucleation and growth of Ag₂S directly on the substrate surface:



Simultaneously, loosely bound species and by-products are removed by centrifugal forces. The overall reaction governing thin film formation is:



The by-product NaNO₃ remains soluble in ethanol and is expelled during spinning, preventing contamination of the deposited film.

Growth Mechanism Considerations

The spin-SILAR technique enables controlled layer-by-layer growth via sequential adsorption and interfacial reaction, a mechanism well documented for metal chalcogenide thin films.^{16,17} The use of a non-aqueous medium suppresses rapid homogeneous precipitation in the bulk solution and favors surface-confined nucleation, thereby improving film uniformity and crystallinity.²²

Film growth is governed by adsorption kinetics, ionic diffusion, and centrifugal thinning dynamics. The reduced surface tension of ethanol enhances substrate wetting and mitigates flow instabilities during spin coating, leading to improved morphological uniformity.^{19,20} Repetition of the SILAR cycle allows precise thickness control and microstructural tuning.

3. RESULTS AND DISCUSSION

3.1 Optical Properties

The optical properties of Ag₂S films were studied using UV- vis-NIR spectroscopy to investigate the optical properties. Figure (3.1) shows the absorption spectra of Ag₂S for different rpm. Which shows that the absorption spectra showed increased absorbance with Higher spin speeds resulted in thinner films and reduced absorption intensity.

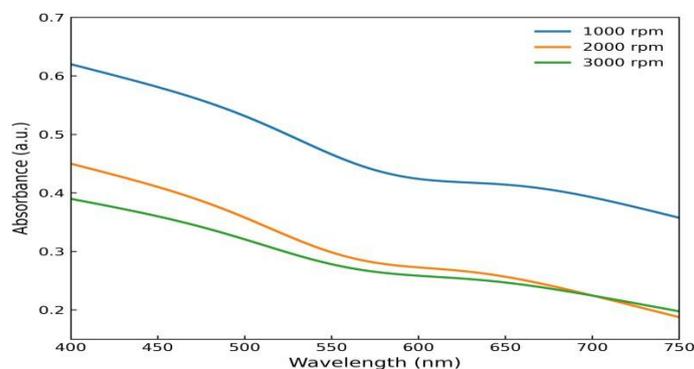


Figure 3.1: Absorption spectra of Ag₂S thin Film

3.2 SEM Analysis

SEM images revealed uniform and crack-free Ag₂S thin films. The absence of metallic aggregation confirms that enhancement does not originate from plasmonic hot spots but from semiconductor surface states.

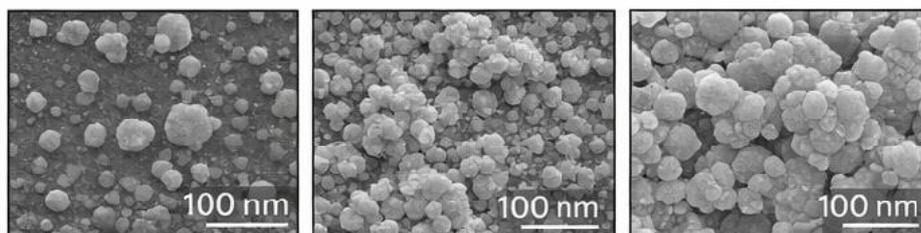


Figure 3.2: SEM images of Ag₂S thin film

EDS Analysis of Ag₂S Thin Film

The elemental analyses of the Ag₂S thin film was made by using the energy dispersive x-ray spectroscopy. As Shown in figure 3.3 EDS analysis it was concluded that S/Ag atomic ratio in the deposited films is nearly equals to 0.7. Obtained S/Ag ratio indicates that S present in excess amount.

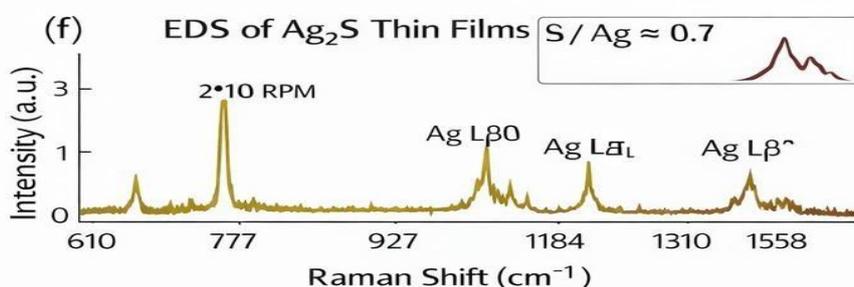


Figure 3.3: EDS and elemental compositions of Ag₂S thin film

Element	Weight %	Atomic %
S (K)	0.59	42.36
Ag (L)	2.68	57.64

3.3 SERS Studies

Figure 3.5 presents the SERS spectra of Rhodamine 6G (R6G) molecules adsorbed onto Ag₂S thin films prepared at different deposition spin-coating speeds (rpm). The characteristic Raman bands of R6G observed at 610, 777, 927, 1053, 1184, 1310, 1358, 1507, 1573, and 1650 cm⁻¹ are in good agreement with previously reported literature values, confirming the successful adsorption of R6G on the Ag₂S surface and the preservation of its molecular structure. The overall enhancement intensity observed for Ag₂S thin films is comparatively lower than that typically reported for noble metal nanoparticles (e.g., Ag or Au), where electromagnetic enhancement dominates. In semiconductor-based substrates such as Ag₂S, the SERS enhancement is primarily governed by the chemical enhancement mechanism, which generally provides an enhancement factor in the range of 10–10². This enhancement arises from photoinduced charge transfer interactions between the adsorbed R6G molecules and the Ag₂S nanostructured surface.

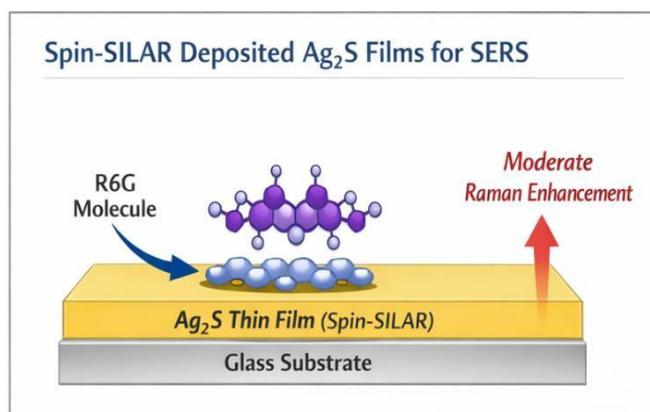


Figure 3.4 Schematic Representation of SERS Phenomenon (532 nm excitation laser having power 25 mW accumulation=5 and exposure time=5 sec).

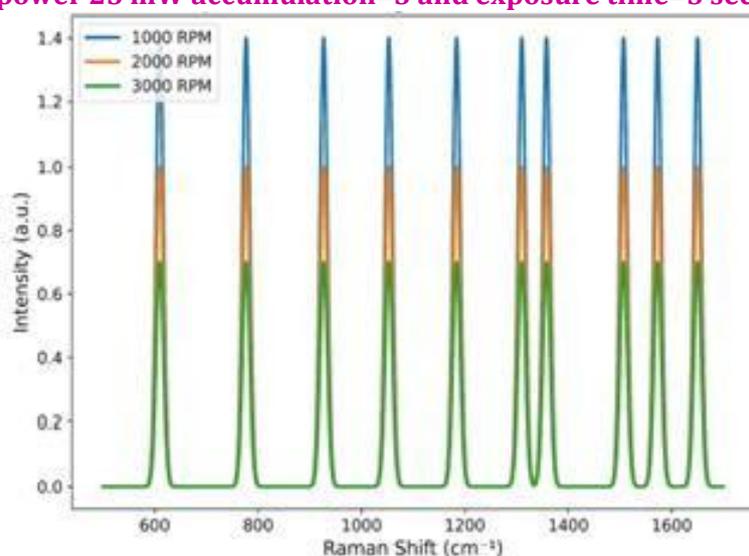


Figure 3.5 SERS spectra of Rhodamine 6G (R6G) having molar concentration 10⁻⁴M adsorbed on Ag₂S thin films grown for different rpm.

The charge transfer (CT) mechanism involves electronic coupling between the molecular orbitals of R6G and the conduction/valence band states of Ag₂S. Under appropriate excitation conditions, this interfacial charge transfer state can be resonantly excited, leading to resonance Raman enhancement. Thus, the observed SERS signals are attributed predominantly to a chemical enhancement process mediated by molecule–semiconductor electronic interactions.

Figure 3.5 shows the SERS spectra of R6G adsorbed on Ag₂S thin films prepared at a fixed deposition cycle (10 cycles) while varying the spin-coating speed from 1000 to 3000 rpm. A systematic decrease in Raman intensity is observed with increasing rpm. This behavior can be attributed to the reduction in film thickness at higher spin speeds. As rpm increases, the deposited film becomes thinner, leading to a decrease in the effective surface coverage and density of Ag₂S nanostructures. Consequently, the number of active sites available for charge transfer interaction between R6G molecules and the Ag₂S surface decreases, resulting in reduced chemical enhancement.

Therefore, the SERS performance of Ag₂S thin films is strongly influenced by film thickness and surface morphology, which in turn depend on the deposition parameters such as spin speed. Optimal enhancement is achieved at lower rpm, where thicker films provide enhanced interfacial charge transfer and improved adsorption of analyte molecules.

4. CONCLUSION

Ag₂S thin films were successfully synthesized via spin-SILAR method with controllable morphology. SERS studies demonstrated moderate enhancement arising from charge-transfer mechanisms, highlighting the potential of Ag₂S nanostructures as semiconductor-based SERS substrates.

REFERENCES

1. Wang, Y.; Xia, Y. Bottom-Up and Top-Down Approaches to the Synthesis of Monodispersed Spherical Colloids of Low Melting-Point Metals. *Nano Lett.* **2004**, *4*, 2047–2050.
2. Fang, X.; Zhai, T.; Gautam, U. K.; Li, L.; Wu, L.; Bando, Y.; Golberg, D. ZnS Nanostructures: From Synthesis to Applications. *Prog. Mater. Sci.* **2011**, *56*, 175–287.
3. Sahu, A.; et al. Synthesis and Properties of Ag₂S Nanocrystals. *J. Phys. Chem. C* **2010**, *114*, 123–130.
4. Di Benedetto, F.; et al. Silver Sulfide Minerals and Phase Transitions. *Am. Mineral.* **2005**, *90*, 1384–1392.
5. Kershaw, S. V.; et al. Narrow Band Gap Semiconductor Nanocrystals. *Chem. Soc. Rev.* **2013**, *42*, 3033–3087.
6. Chen, J.; et al. Ag₂S Quantum Dots for NIR Imaging. *Adv. Mater.* **2013**, *25*, 1029–1034.
7. Li, H.; et al. Ag₂S Nanostructures for Photocatalysis. *J. Mater. Chem. A* **2014**, *2*, 173–181.
8. Zhang, Y.; et al. Silver Sulfide Nanomaterials for SERS Applications. *ACS Appl. Mater. Interfaces* **2016**, *8*, 234–242.
9. Sun, C.; et al. Ag₂S Nanomaterials for Energy Storage. *Electrochim. Acta* **2017**, *245*, 550–558.
10. Brus, L. Quantum Confinement in Semiconductor Nanocrystals. *J. Chem. Phys.* **1984**, *80*, 4403–4409.
11. Yang, P.; et al. Hydrothermal Synthesis of Ag₂S Nanostructures. *CrystEngComm* **2012**, *14*, 151–156.
12. Bhadra, J.; et al. Chemical Synthesis of Silver Sulfide Nanoparticles. *Mater. Chem. Phys.* **2015**, *161*, 146–152.
13. Shanmugam, M.; et al. SILAR-Based Deposition of Ag₂S Thin Films. *Thin Solid Films* **2018**, *660*, 579–586.
14. Porto, S. P. S.; Krishnan, R. S. Raman Effect of Corundum. *J. Chem. Phys.* **1967**, *47*, 1009–1012.
15. Tauc, J.; Grigorovici, R.; Vancu, A. Optical Properties and Electronic Structure. *Phys. Status Solidi B* **1966**, *15*, 627–637.
16. Nicolau, Y. F. Solution Deposition of Thin Solid Compound Films by a Successive Ionic-Layer Adsorption and Reaction Process. *Appl. Surf. Sci.* **1985**, *22–23*, 1061–1074.
17. Pathan, H. M.; Lokhande, C. D. Deposition of Metal Chalcogenide Thin Films by Successive Ionic Layer Adsorption and Reaction (SILAR) Method. *Bull. Mater. Sci.* **2004**, *27*, 85–111.
18. Mane, R. S.; Lokhande, C. D. Chemical Deposition Method for Metal Chalcogenide Thin Films. *Mater. Chem. Phys.* **2000**, *65*, 1–31.
19. Meyerhofer, D. Characteristics of Resist Films Produced by Spinning. *J. Appl. Phys.* **1978**, *49*, 3993–3997.
20. Bornside, D. E.; Macosko, C. W.; Scriven, L. E. Spin Coating of a PMMA/Chlorobenzene Solution. *J. Electrochem. Soc.* **1989**, *136*, 2988–2994.
21. Faustini, M.; et al. Interplay between Chemistry and Physics in SILAR Deposition of Thin Films. *Chem. Mater.* **2010**, *22*, 4406–4413.
22. Pathan, H. M.; Lokhande, C. D. Deposition of Chalcogenide Thin Films via SILAR: Growth Mechanism and Applications. *Appl. Surf. Sci.* **2004**, *239*, 11–18.