

FABRICATION OF SILVER BISMUTH SULFIDE THIN FILMS VIA Ag/Bi STACK PHYSICAL VAPOR DEPOSITION AND SULFURIZATION

Aistis Melnikas¹, Marta Miró Llorente², Diego Nistal Castro², Victoria Rotaru², Alex López García², Alejandro Perez-Rodriguez^{2,3}, Skirma Žalėnienė¹, Pedro Vidal Fuentes²

¹Kaunas University of Technology, Department of Physical and Inorganic Chemistry, Kaunas, Lithuania

²Catalonia Institute for Energy Research (IREC), Jardins de les Dones de Negre 1, 2^a pl., 08930 Sant Adrià del Besòs Barcelona, Spain

³Universitat de Barcelona, Departament d'Enginyeria Electrònica i Biomèdica, IN2UB, C/ Martí i Franqués 1, 08028 Barcelona, Spain
aistis.melnikas@ktu.edu

Silver bismuth sulfide (AgBiS₂) has recently emerged as a promising, non-toxic light absorber material for thin-film photovoltaic applications due to its suitable optoelectronic properties and earth-abundant elemental composition [1]. AgBiS₂ has demonstrated exciting potential to be used in photovoltaics, as solar cells employing silver bismuth sulfide have achieved power conversion efficiencies exceeding 9% [2]. Many current methods of AgBiS₂ deposition rely on advanced and complex technology, such as atomic layer deposition (ALD), while physical vapor deposition routes offer reproducibility, low manufacturing costs, and an industrially applicable procedure. This opens the door to further optimize this technology through a larger and scalable process.

In this research, we investigate the growth of AgBiS₂ by employing physical vapour deposition routes. Glass substrates were first coated with molybdenum (Mo) by thermal evaporation, which acts as a back contact, onto which all films were subsequently deposited. Additionally, the formation of a MoS₂ layer beneath the absorber film during sulfurization can be beneficial by serving as a hole transport layer if properly optimized. Layers of silver (Ag) and bismuth (Bi) were deposited by e-beam evaporation and thermal evaporation, respectively. The Ag/Bi stack sequence, ratio, and total thickness were varied. The silver layer thicknesses of 6.5, 9.5, and 19 nm and the bismuth layer thicknesses of 13.7, 20, and 40 nm were employed, corresponding to the total stack thicknesses in the range of 20.2–69 nm, while expecting the AgBiS₂ thickness in the range of 35–100 nm. All layers were obtained on 1.5 x 2 cm² substrates. Furthermore, large area 5 x 10 cm² samples were fabricated by fixing the thickness of one metal layer while depositing a thickness gradient of the other (Ag or Bi). Large-area samples were employed to investigate the effect of the Ag/Bi stack ratio. Sulfurization of the deposited stacks was subsequently carried out as a reactive annealing in a tubular furnace over a temperature range of 300–500 °C for 30 min.

All samples were characterized by X-ray diffraction (XRD) analysis, Raman spectroscopy, and Scanning Electron Microscopy (SEM). XRD analysis reveals crystalline and preferred phases of AgBiS₂ with no significant influence in the Ag/Bi versus Bi/Ag sequence, Raman spectroscopy suggests the formation of MoS₂ at temperatures of 450 and 500 °C, and SEM analysis indicates homogenous film morphology in thicker stacks.

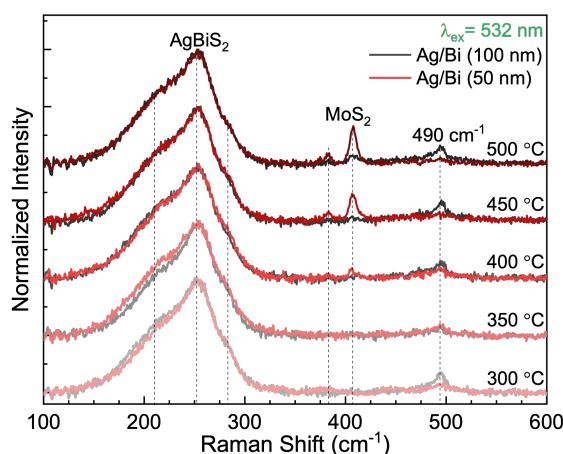


Fig. 1. Raman spectroscopy measurement of different AgBiS₂ samples fabricated by using different thicknesses of Ag/Bi precursor stacks and annealed at different temperatures

[1] U. Chalapathi et al., "Synthesis of AgBiS₂ films by sulfurizing Bi/Ag stacks for thin film photovoltaics," *Optical Materials*, vol. 152, p. 115492, May 2024, doi: 10.1016/j.optmat.2024.115492.

[2] Y. Wang, S. R. Kavanagh, I. Burgués-Ceballos, A. Walsh, D. O. Scanlon, and G. Konstantatos, "Cation disorder engineering yields AgBiS₂ nanocrystals with enhanced optical absorption for efficient ultrathin solar cells," *Nature Photonics*, vol. 16, no. 3, pp. 235–241, Feb. 2022, doi: 10.1038/s41566-021-00950-4.