

Supporting Information

Single molecular precursor ink for AgBiS₂ thin films: synthesis and characterization

Ening Gu*^{1, 2 †}, Xianzhong Lin^{1, 3 †}, Xiaofeng Tang^{1, 2}, Gebhard J. Matt*¹, Andres Osvet¹, Yi Hou¹, Sebastian Jäger⁴, Chen Xie¹, André Karl¹, Rainer Hock⁵ and Christoph J. Brabec*^{1, 4}

¹Institute of Materials for Electronics and Energy Technology (i-MEET), Department of Materials Science and Engineering, Friedrich-Alexander-Universität Erlangen-Nürnberg, Martensstraße 7, 91058 Erlangen, Germany

²Erlangen Graduate School in Advanced Optical Technologies (SAOT), Paul-Gordanstraße 6, 91052 Erlangen, Germany

³School of Materials Science and Engineering, Sun Yat-sen University, Guangzhou 510275, PR China

⁴Bavarian Center for Applied Energy Research (ZAE Bayern), Immerwahrstraße 2, 91058 Erlangen, Germany

⁵Chair for Crystallography and Structural Physics, Friedrich-Alexander-University Erlangen-Nürnberg, Staudtstrasse 3, 91058, Erlangen, Germany

† These authors contributed equally to this work

* Correspondence should be addressed to:

C.J.B. (christoph.brabec@fau.de)

G.J.M (gebhard.matt@fau.de)

E.G. (ening.gu@fau.de)

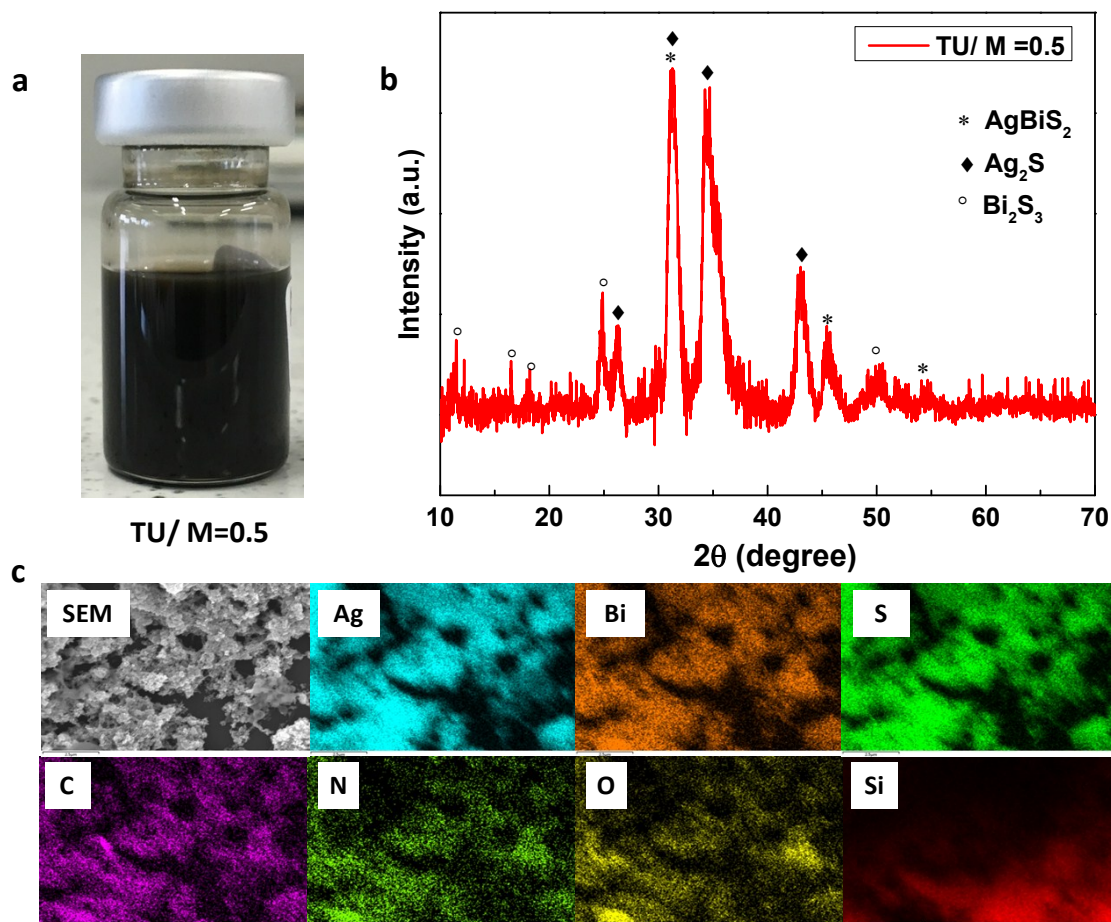


Figure S1 a) Digital graph of TU/M= 0.5 solution. b) Room temperature XRD pattern of precipitates from solution. We centrifuged and washed the solution (10000 rpm, 10 min) 2 times, and re-dispersed precipitates inside isopropanol, and drop-casted onto glass, and then measured the XRD. There might be AgBiS₂, Ag₂S and Bi₂S₃ inside. c) EDX mapping of precipitates on Si substrate. The precipitates include Ag, Bi, S, C, N and O elements. O might come from environment contamination, C and N might result from the organic residues.

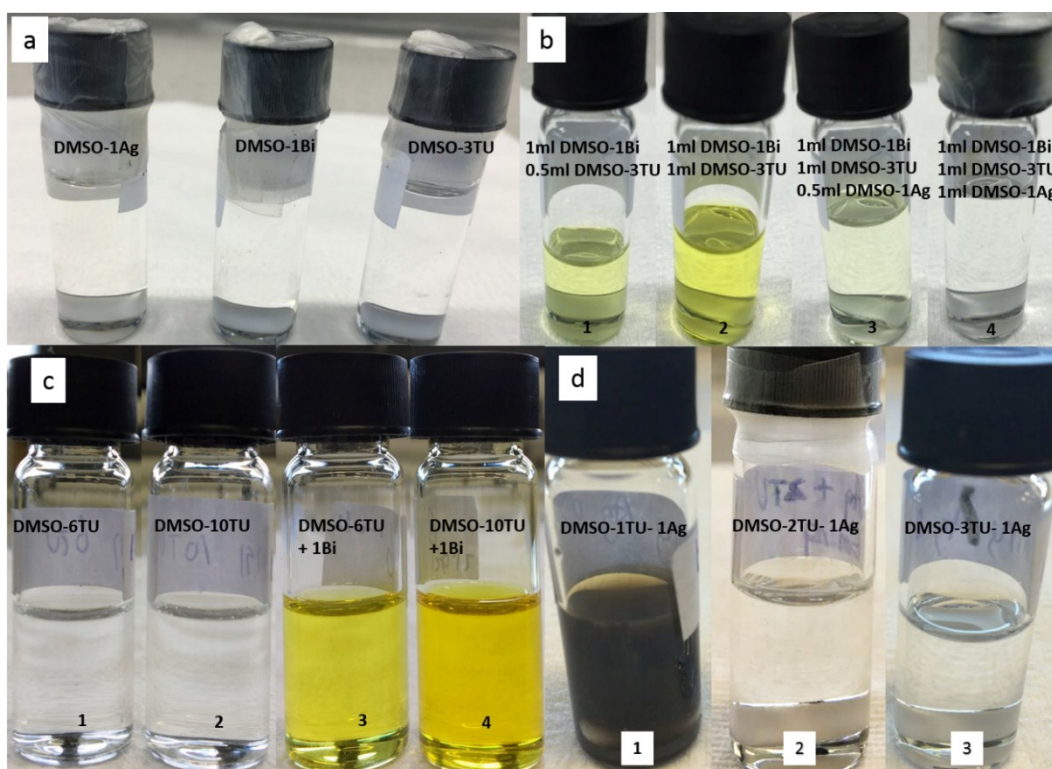
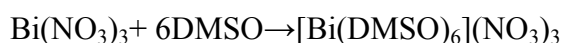


Figure S2 a) Digital graphs of pure DMSO-1Ag, DMSO-1Bi, DMSO-3TU solutions. 1Ag, 1Bi and 3TU stand for the molar concentration of Ag, Bi and TU are 0.13 M, 0.13 M and 0.39 M, respectively. Pure DMSO and those three solutions are all colourless and transparent. b) Graphs show colour change after mixing certain amount solutions exhibited in figure S2-a. Procedure: DMSO-3TU solution was added inside 1 ml DMSO-1Bi solution drop wise. When we added 200 μ l DMSO-3TU solution, the colour started turning to light yellow, colour of 1 ml DMSO-1Bi + 0.5 ml DMSO-3TU is shown as b-1. Further increasing the amount of DMSO-3TU solution, the yellow colour became darker, shown as b-2. When we added DMSO-Ag solution inside drop wise, the yellow colour became lighter and lighter, like b-3. When we added 1 ml DMSO-Ag, the final solution is colourless and transparent again. Note that solutions were kept stirring during the mixing procedure. c) When we add 6TU or 10TU inside

DMSO, the solution is colourless, shown as c-1 and c-2. After adding 1Bi inside in both 6TU and 10TU DMSO solution, the colour became yellow, shown as c-3 and c-4. The one with 10TU is darker. d) DMSO-1TU-1Ag solution is dark brown, while DMSO-2TU-Ag and DMSO-3TU-Ag solution are colourless.

Proposed chemical reactions below show the coordination states between TU, Ag⁺, Bi³⁺ and DMSO, discussion is based on the results from XRD, Raman, and visual colour change of the inks.

Silver-free ink

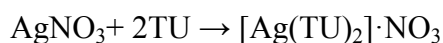


$[\text{Bi}(\text{DMSO})_6](\text{NO}_3)_3$ is colourless, while $[\text{Bi}(\text{DMSO})_6](\text{NO}_3)_3\text{-TU complex}$ is yellow, more TU inside, the colour is darker.

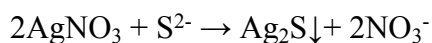
Bismuth-free ink (insufficient TU and sufficient TU)

When the TU amount is not enough ($[\text{TU}] / [\text{Ag}] \leq 1$), reaction gives Ag₂S precipitates. When $[\text{TU}] / [\text{Ag}] \geq 2$, the solution is colourless.

Soluble complex when TU is sufficient:

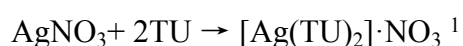
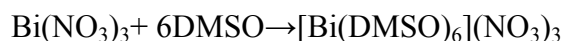


Insoluble precipitates when TU is insufficient:



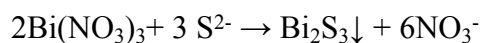
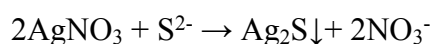
Silver- Bismuth-TU-DMSO combined ink (insufficient TU and sufficient TU)

Soluble complex when TU is sufficient:

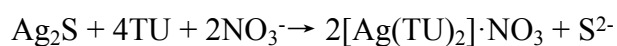


Whether $[\text{Ag}(\text{TU})_2] \cdot \text{NO}_3$ and $[\text{Bi}(\text{DMSO})_6](\text{NO}_3)_3\text{-TU}$ inside the precursor will further form a Ag-Bi-TU-DMSO combine complex net is unclear. Discussions in this work assume they exist separately.

Insoluble precipitates when TU is insufficient:



The reaction is reversible. The dark solution can slowly turn to clear precursor after adding more TU inside, confirmed by experiment, shown as Figure S3. Note that the reaction is real slow.



Besides, when all materials and DMSO were added inside the vial without stirring, we discovered that part of the solution become dark first. As dissolution rate of each component is different, without external assistive stirring, there exists

competitive reaction, AgNO_3 react with TU preferentially. What's more, according to the colour change in S2-b, we consider that Ag is coordinated to TU.

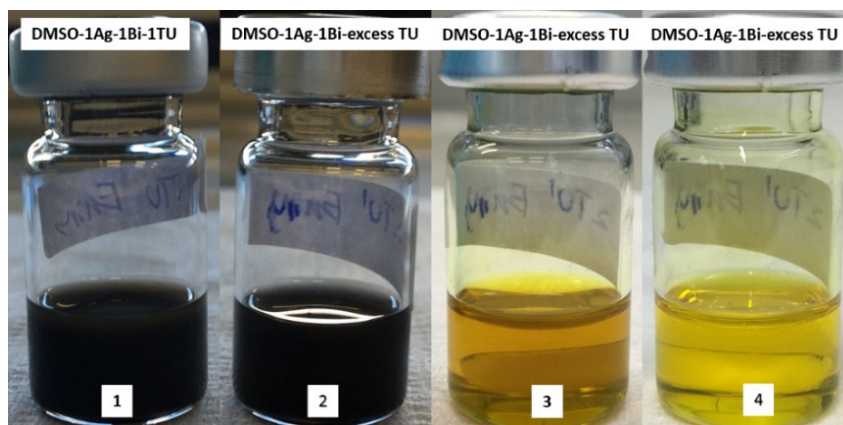


Figure S3 1) graph of DMSO-1Ag-1Bi-1TU solution. It started to become dark after stirring around 10 min. 2) when 2TU was added inside, and it was quite dark after 3h stirring. Then we added excess amount of TU inside, and kept the solution stirring. 3) After one days' stirring, it become dark yellow, and there existed visible particles inside. 4) After two days' stirring, the solution was clear again. The yellow colour results from excess TU and its complexation with metal ion. This result confirms that TU has a crucial impact on forming stable molecular ink.

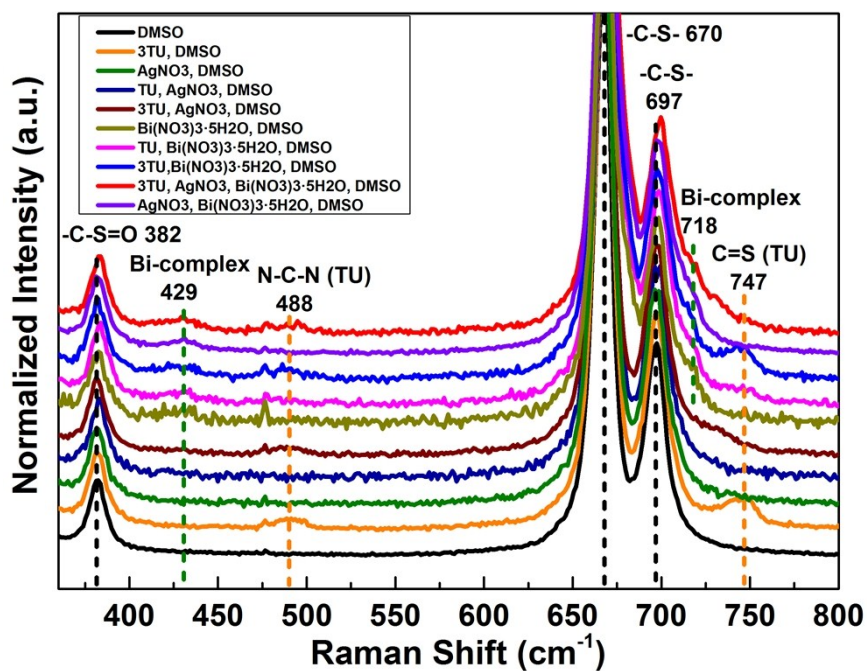


Figure S4 Raman spectra of different Ag-Bi-n·TU-DMSO inks and reference

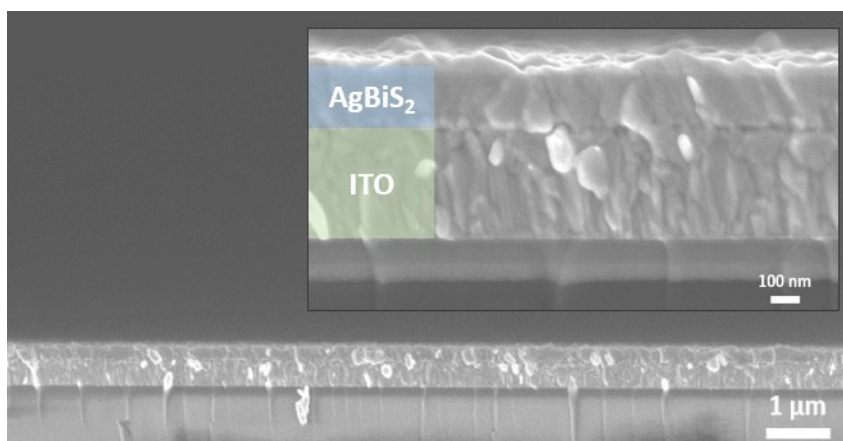


Figure S5 Cross section micrograph of AgBiS₂ films obtained from TU/M = 1.5 precursor and annealed at 300 °C for 40 min in N₂.

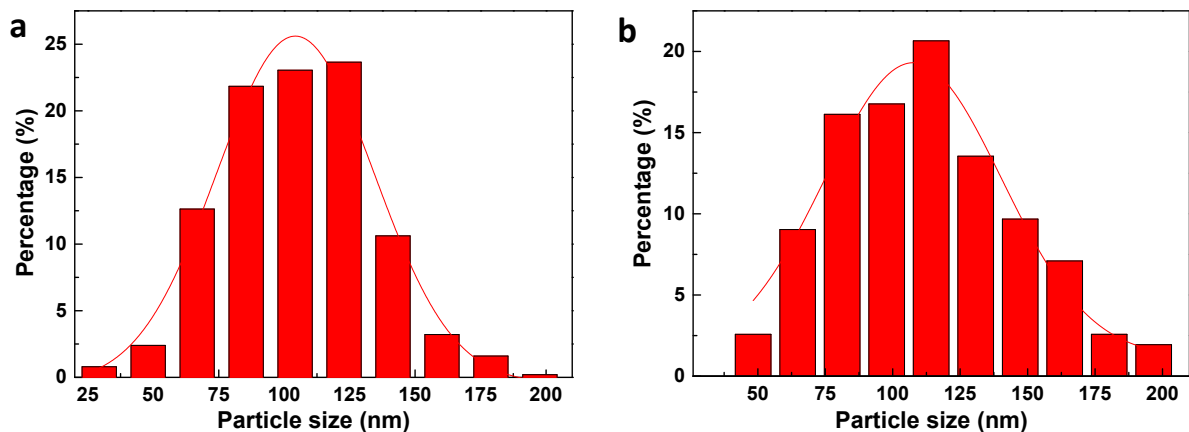


Figure S6 a) Histogram of particle size distribution obtained from SEM (Figure 4-d), average size is around 105 nm, b) Histogram of particle size distribution obtained from AFM (Figure 4-e), average size is around 112 nm.

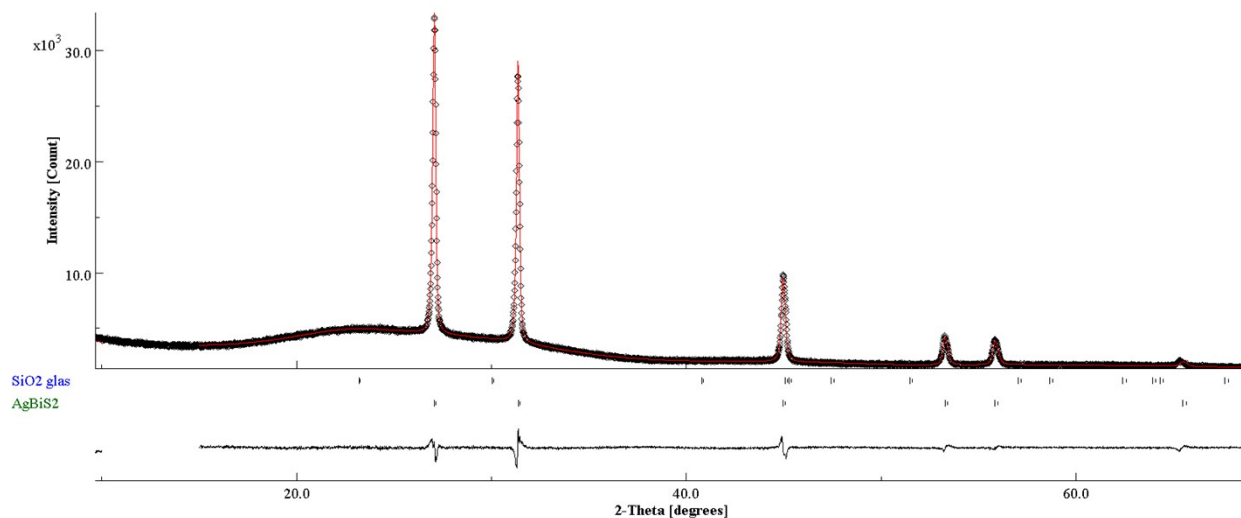


Figure S7 Powder diffraction pattern of synthesized AgBiS_2 (TU/M = 1.5 and annealed at 300 °C). The scattering from crystalline AgBiS_2 was modelled in space group Fm-3m (diamond symbols). Shown is the corresponding Rietveld fit to the data (continuous line) and difference plot shown in the inset below. To model the scattering from the

SiO₂ glass substrate, a crystalline SiO₂ phase was fitted with a crystallite size of about a unit cell. This resembles well the amorphous scattering contribution from the glass.

Fitting procedure: Scattering from a cubic AgBiS₂ phase, crystallized in space group Fm-3m (rock salt structure)² with a statistical distribution of Ag and Bi on Wyckoff site 4a (0,0,0,) and sulphur on site 4b (1/2,1/2,1/2) was fitted to the measured scattering pattern with the program MAUD³. The background was modelled by a scattering contribution of amorphous SiO₂ and a polynomial function. The AgBiS₂ diffraction shows a preferred orientation of the crystallites, which was best modelled assuming a fibre texture with axis [111] perpendicular to the substrate surface. A thin film correction was applied. The fitted cubic lattice parameter *a* of AgBiS₂ is 5.698(2) Å.

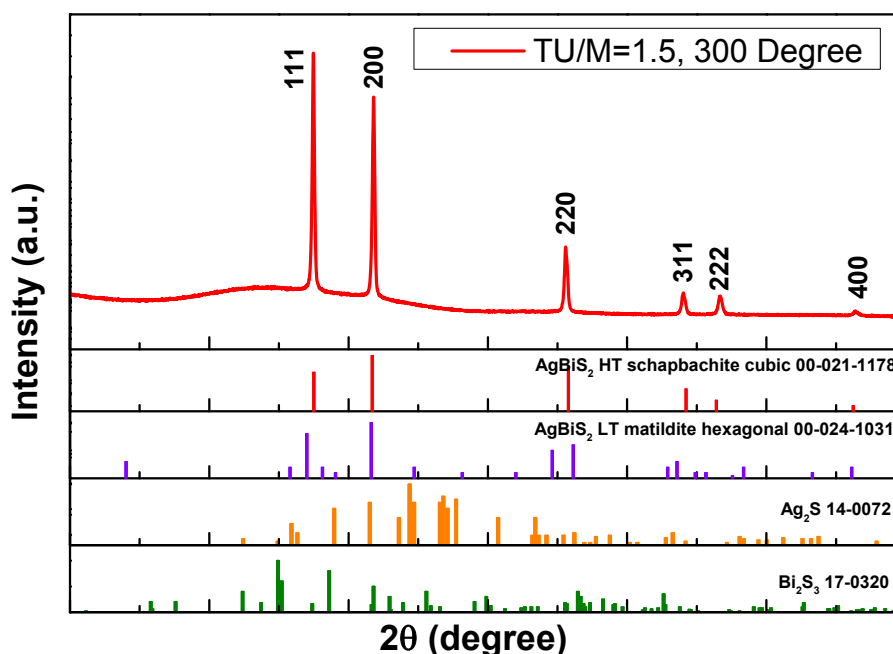


Figure S8 XRD pattern of TU/M = 1.5, 300 °C post annealed sample

It has been reported that AgBiS_2 has two different phases, a high temperature cubic phase called Shapbachite and a low temperature hexagonal phases called Matildite⁴⁻⁶. By fitting and detailed peak assignments, we claim that the phase of the synthesized AgBiS_2 film is pure cubic AgBiS_2 phase with the preferred orientation in [111] direction, corresponding texture fitting is shown in Figure S9.

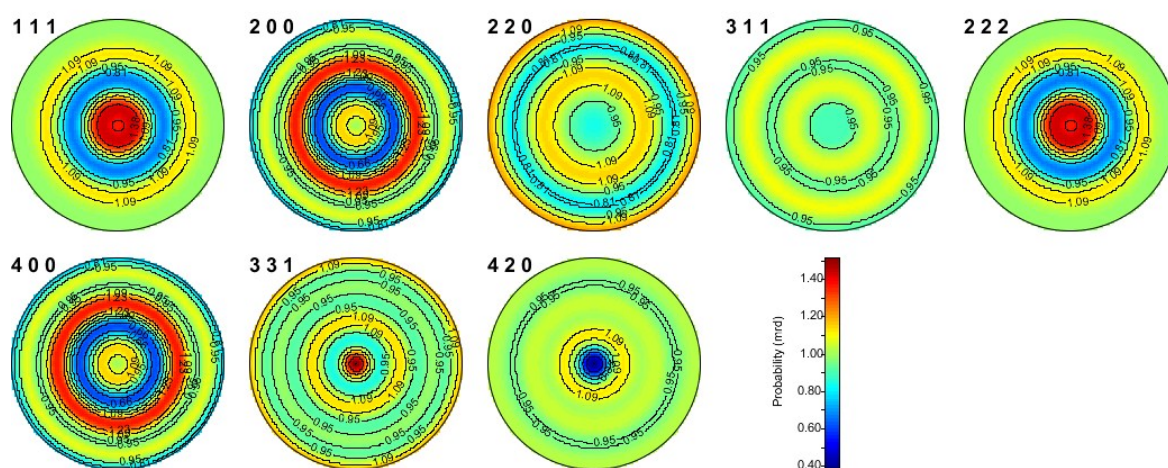


Figure S9 Texture plot of the powder pattern from the same AgBiS_2 , showing the [111] fibre texture modelling best the measured Bragg intensities.

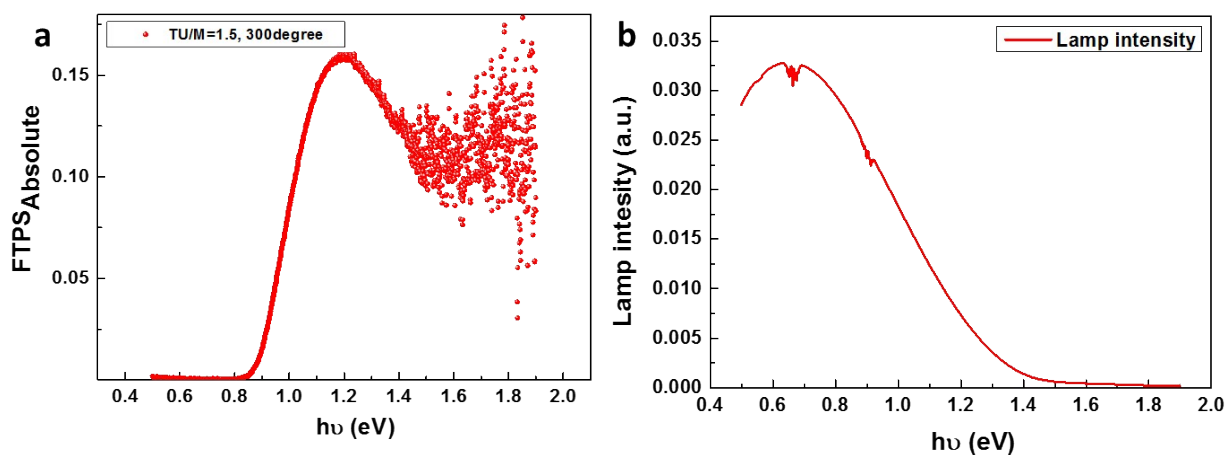


Figure S10 a) FTPS photocurrent spectrum of the TU/M=1.5, 300 °C annealed sample.

The noise at higher energy range results from the relative low lamp intensity, as shown in b).

It might due to the relative low light intensity of our lamp in high energy range, the FTPS data could not reflect absorption character properly and give quite noisy data. Direct Tauc plot of FTPS spectrum doesn't give reasonable fitting.

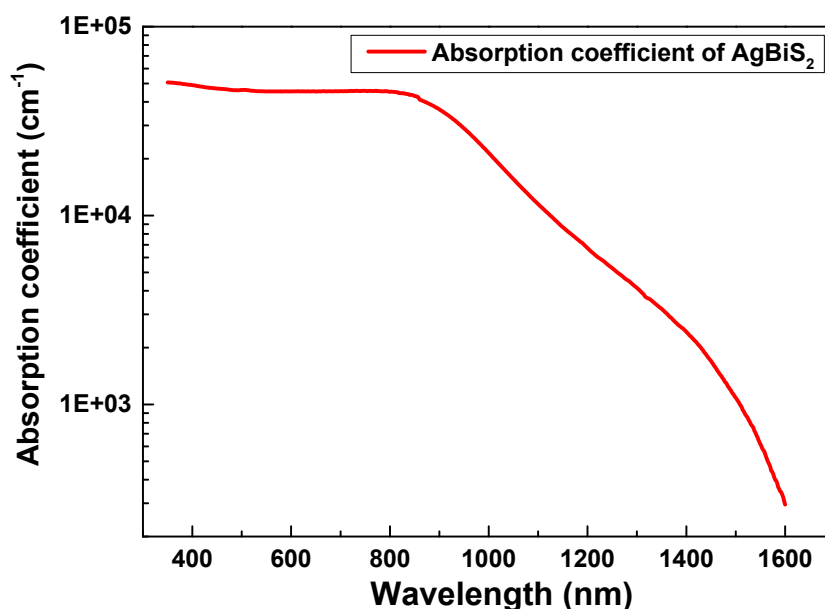


Figure S11 Absorption coefficient of the obtained AgBiS₂ thin film.

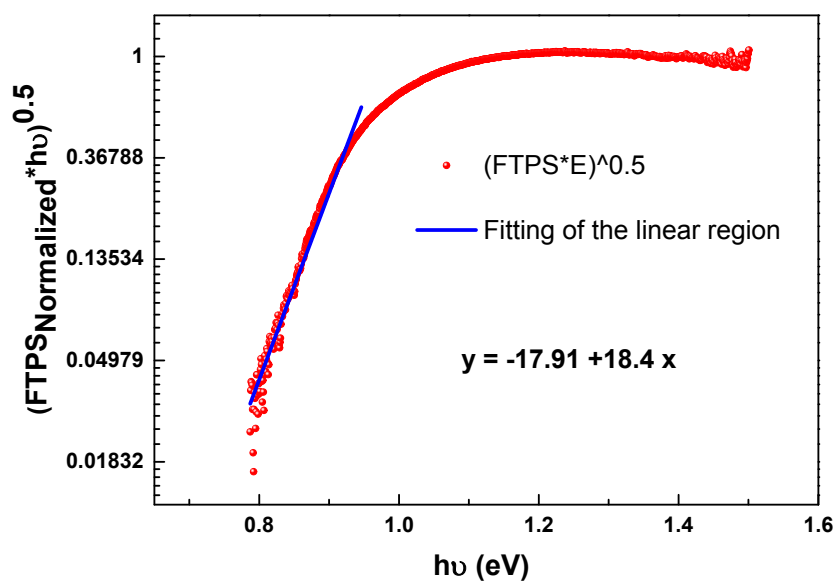


Figure S12 Linear fitting of the lower energy part of indirect Tauc plot of the FTPS spectrum in semilogarithmic scale.

Reference

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