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Ultra-Thin Absorber Layers of Silver Bismuth Sulfide from Molecular Precursors

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ABSTRACT

Here we present a robust molecular precursor-based approach to synthesize high quality thin films of silver bismuth sulfide (AgBiS_2). Pure phase cubic AgBiS_2 thin films are prepared, which are smooth and dense down to thicknesses less than 40 nm. Comprehensive structural and morphological analysis of the as-prepared films as a function of processing temperature and composition is presented, including X-ray diffraction, X-ray photoelectron spectroscopy and Scanning Electron Microscopy. The optical properties of the films and their electronic band structure are also presented. The as-prepared films showing impressive light absorption properties with absorption coefficients reaching 10^5 cm^{-1} for energies above c.a. 950 nm. Finally, their photoactivity is demonstrated through photoconductivity measurements on lateral electrodes. The methods outlined herein enable the fabrication of AgBiS_2 semiconductor thin films at low processing temperatures (150 °C) with a dense morphology and tunable Ag:Bi composition. Such films provide an excellent platform for the fabrication of AgBiS_2 -based optoelectronic devices and solar cells.

INTRODUCTION

Solution processing is a powerful and versatile approach for achieving thin film materials with tailored composition, morphology and functional properties.^{1,2,3,4,5,6} As such, it has been widely investigated for myriad applications, including sensing, catalysis, optoelectronics, energy conversion, and storage.^{7,8,9,10,11,12,13} Traditionally, solution processing has utilized chemical bath deposition and electrochemical deposition.^{14,15,16,17,18} Colloidal nanocrystal (NC) have also been extensively used, wherein the desired NCs are first synthesized and subsequently formulated into an “ink” suitable for thin film deposition.^{8,19,20,21,22,23} Recently, research in the area of solution processed thin films has received increasing focus on the use of molecular metal–organic complexes, termed molecular precursors (MP). The MP approach entails the formulation of a solution containing discrete precursors that can be readily cast into a thin film and then decompose upon heating to form the desired compound and crystal phase.^{24,25}

During its inception, the field of MPs was mainly focused on metal oxides, with sol-gel approaches having been used for decades for the fabrication of thin films and porous materials for a variety of applications.^{26,27,28} In recent years, molecular precursors have been extended to the synthesis of semiconducting chalcogenide materials, especially metal sulfides. For example, the Mitzi *et. al* pioneered the use of hydrazine as a solvent to dissolve simple metal chalcogenides for the synthesis of $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) thin films.⁵ An alternative method by the group of Hillhouse investigated metal-thiourea complexes in coordinating solvents such as DMSO for the synthesis of a variety of sulfides, including CZTS and $\text{CuIn}_x\text{Ga}_{(1-x)}\text{S}_2$ (CIGS).²⁹ The group of Brutchey developed a solvent mixture based on ethylenediamine and short-chain thiols able to dissolve a large variety of metal salts, which was then used to deposit thin films that convert to pure metal chalcogenides upon heating.³⁰ Additional approaches have also been proposed, showing the large potential of molecular precursors for the synthesis of a wide range of semiconducting materials.^{31,32}

To frame the current work, we note that the current competitive approach to the use of MPs is colloidal nanocrystal (NC) inks. The MP and NC approaches have both advantages and disadvantages. Through surface engineering, NC inks typically have lower organic:inorganic ratios compared to their MP analogues and offer greater control over crystal domain size and shape. However, this comes at the cost of a longer, more complex synthetic processes (for both nanocrystal synthesis and ink formulation), great difficulty with scale-up, and in the case of ternary and quaternary NCs, poor or no control over the final crystal composition.³³ Molecular precursor strategies are more versatile and flexible, enabling access to a wider range of materials (including those yet to be successfully synthesized as nanocrystals), and at the same time involve simpler scalable synthetic processes with highly accurate compositional control. Recent progress in the field has shown that materials of the highest quality can be fabricated from MPs, laying the foundation for the adoption of such precursors for the manufacture of efficient devices.^{7,29}

Over the past few years the material silver bismuth sulfide (AgBiS_2) has received renewed attention as an absorber layer for photovoltaic applications, with extremely promising initial results.^{34,35,36,37} AgBiS_2 is a I-III-VI₂ semiconductor comprised of non-toxic elements with desirable optoelectronic properties, including a narrow band gap at around 1.1-1.2 eV and a large absorption coefficient ($\sim 10^5 \text{ cm}^{-1}$ in the visible spectral range).^{38,39} Prior work on AgBiS_2 includes the solid-state synthesis of single crystal ingots, sequential ionic layer adsorption reaction (SILAR) techniques, solvothermal methods, microwave synthesis and colloidal nanocrystals.^{34,40,41,42,35,36,39,43}

To date there exists only a single work (from the Brabec group) demonstrating the fabrication of AgBiS_2 thin films through the use of MPs.³⁸ We note here that the thiourea method outlined therein was shown to be limited to fabrication temperatures above 250 °C and film thickness above 200 nm. Importantly, prior investigations into the fabrication of solar cells

from both spin-coated and spray coated AgBiS₂ nanocrystal-based solutions has revealed that low processing temperatures (100–150 °C) and films with thickness below c.a. 60 nm are critical to achieving high performing solar cell devices.^{36,35,37,44} While the optimized thin films from the aforementioned thiourea-based precursors display excellent qualities, the required processing conditions fall clearly outside of these optimal film and processing parameters for AgBiS₂. This raises legitimate concern as to the flexibility and suitability of such methods for generating thin films appropriate for device incorporation. In light of these current limitations, it remains highly desirable to develop alternative methods to AgBiS₂ NCs that are able to produce device quality ultra-thin films at low processing temperatures.

Here we report for the first time a robust and reproducible MP approach to synthesize high (device) quality thin films of AgBiS₂ with tunable thicknesses to below 40 nm. Metal-dithiocarbamate (DTC) complexes of silver and bismuth were synthesized and used to fabricate AgBiS₂ thin films via spin coating. Our approach leverages off the low decomposition temperatures of metal–DTC complexes and circumvents the need for the prior synthesis of AgBiS₂ NCs, while providing accurate control over Ag:Bi stoichiometry, retaining excellent tunability of film thickness, and access to processing temperatures as low as 150 °C.

Comprehensive structural and morphological analyses of the as-prepared films as a function of both processing temperature and Ag:Bi composition are presented, including X-ray diffraction, X-ray photoelectron spectroscopy and Scanning Electron Microscopy. The optical properties of the films and their electronic band structure are also presented. Finally, their photoactivity is demonstrated through photoconductivity measurements, validating their use as photodetectors and light absorbing layers for photovoltaic applications.

RESULTS AND DISCUSSION

The synthetic method outlined herein involves the dissolution of silver and bismuth precursors in dithiocarbamic acid (DTCA) to form metal dithiocarbamate complexes. During the optimization process for the molecular precursors several different metal salts and solvent combinations were investigated. Metal acetates, metal chlorides and metal oxides as precursor salts for metal–DTC complexes, in conjunction with solvents, such as ethanol, 2-methoxyethanol, DMF, DMSO, pyridine, γ -butyrolactone, and methyl ethyl ketone were all trialed. Furthermore, combinations of the aforementioned solvents were also tested to assist film formation where required. The constraints were that the final MP be stable, achievable in reasonable concentrations (~ 0.1 M), optically transparent (non-scattering), and have excellent film forming properties (as required to make ultra-thin films). It was found that silver acetate and bismuth oxide in pyridine was the only combination that fulfilled all these criteria. For details of the MP synthesis see the Experimental Section. The final optimized precursor the solutions can be then mixed in the desired ratio and diluted appropriately for thin film deposition.

To investigate the effect of processing (decomposition/annealing) temperature, thin films were fabricated by spin coating a metal-DTC solution with an Ag: Bi molar ratio of 1:1 and heated at different temperatures in a nitrogen-filled glove box (see Experimental section for details). Figure 1 shows the X-ray diffraction (XRD) patterns for thin films processed between 150 °C and 400 °C. Analysis of the XRD confirmed highly crystalline, cubic phase AgBiS₂ without any additional impurities for all the temperatures investigated. All diffraction peaks are an excellent match to the cubic schapbachite phase of AgBiS₂ (space group *Fm3m*, reference ICDD No. 21-1178). Importantly, pure phase, highly crystalline AgBiS₂ was observed for decomposition (annealing) temperatures as low as 150 °C. Trials at lower temperatures resulted in extremely slow decomposition and were unable to effectively produce

high quality thin films. Close inspection of Figure 1 reveals a slight preferential orientation of AgBiS₂ crystals along the $\langle 111 \rangle$ direction. This was also observed recently for AgBiS₂ films fabricated from metal nitrates and thiourea precursors.³⁸ In light of this, the texture coefficient¹⁵ of the as-prepared AgBiS₂ was calculated and the films were found the degree of orientation along the $\langle 111 \rangle$ direction to be between 20–30%. The preferential orientation was found to be fairly consistent across the investigated temperature range (see Table S1 in SI for details on the texture coefficient). In contrast, when depositing AgBiS₂ by simple drop-casting of the precursor solution onto hot substrates, the orientation is lost and the diffraction peak intensity matches the tabulated values for randomly oriented materials (Figure S1). This suggests that the spin coating technique and the subsequent decomposition of the precursor as a thin film is responsible for the preferential orientation of the growing AgBiS₂ crystals.

Figure 1. XRD patterns for ABS samples annealed at temperatures between 150 °C and 400 °C. The predicted diffraction peak positions for cubic AgBiS₂ (ICDD No. 21-1178), and details of the crystalline unit cell are also reported.

To estimate the average crystallite size of the prepared AgBiS₂ we fitted the diffraction peaks with Lorentzian functions and extrapolated the domain size from the full width at half maximum (FWHM) through the Scherrer relationship (see Figure S2 for details). A progressive sharpening of the diffraction peaks and an increase in crystallite size from ~20 nm at 150 °C to

~40 nm at 400 °C, consistent with temperature-induced grain growth (Figure S1). From scanning electron microscopy (SEM) the size of the crystalline grains as a function of temperature follow the same trend as the sizes extrapolated from the XRD patterns. Small, spheroidal AgBiS₂ crystals are observed at (150 °C), which evolve into larger, more faceted crystals with increasing annealing temperatures up to (400 °C) (see Figure S3).

The MP method outlined herein enables facile tuning of the final compounds stoichiometry simply by changing the ratio of the silver and bismuth solutions. In order to evaluate the tolerance of the AgBiS₂ crystal to deviations from the ideal stoichiometry, i.e. either bismuth-rich or silver rich, we systematically varied the volume (mole) ratios of the precursors from 2:1 (Ag:Bi) through to 1:2 (Ag:Bi). As shown in Figure 2 pure cubic AgBiS₂ was obtained for compositions with up to 40% excess of either metal (Ag:Bi = 1:1.4 – 1.4:1). From these data it is evident that the AgBiS₂ structure is remarkably tolerant to variations in stoichiometry, which is likely a consequence of the fact that Ag and Bi reside at the same cation site (alternating atom type) within the cubic crystal.

The ability to change the metal ratio while keeping the desired crystalline phase is often vital to enhance the optoelectronic properties of semiconductor materials. This is especially true for ternary and quaternary chalcogenide materials. For example, stoichiometric CuZnSnS₄ (CZTS) have far poorer charge transport properties and lower efficiencies as solar cells than their copper deficient and zinc rich analogues.^{19,45,46} Likewise, CuIn(Ga)S₂ (CIGS) solar cells have optimal device performances at specific indium/gallium stoichiometry.⁴⁷ The ability to tune the Ag:Bi composition of AgBiS₂ thin films, as demonstrated here, is highly favorable and provides the possibility to precisely tune its semiconducting characteristics through a wide range of stoichiometric adjustments. Increasing the excess of either metal beyond 40% causes the formation of additional phases, Ag₂S (ICDD No. 14-0072) for Ag-rich compositions

(circles), and AgBi_3S_5 (ICDD No. 83-2051, triangles) and pure Bi_2S_3 (ICDD No. 75-1306, stars) for Bi-rich compositions. Notably, when using either pure Bi-DTC or Ag-DTC precursor solutions, pure phase Bi_2S_3 and Ag_2S could also be achieved (see Figure S4).

Figure 2. XRD patterns of AgBiS_2 samples prepared varying the composition of the metal-DTC precursors resulting in mixtures with mole ratios from Ag:Bi 2:1 to Ag:Bi 1:2. Reference patterns for the target phase and impurity phases are reported at the bottom for reference. The annotations highlight the presence of impurities (Ag_2S , circles; AgBi_3S_5 , triangles and Bi_2S_3 , stars).

Having demonstrated the phase purity of our AgBiS_2 films, their oxidation states and the chemical nature of the bonds within the semiconductor as a function of processing temperature were investigated using XPS. We obtained clear signatures for all the elements

constituting AgBiS₂. To rule out the effects of charging on the binding energies (BE) we measured the carbon (C 1s) signal for each sample. A clear signal peak at 284.8 eV was obtained in each case and as such no BE corrections were required (Figure S5). Figure 3 shows the survey spectra and corresponding high-resolution spectra for the elements Ag, Bi and S as a function of temperature. From the survey spectra we see the presence of the expected elements (Ag, Bi, S) as well as the additional presence of trace carbon and oxygen and signal from the substrate (see Figure S5 for details). Importantly, no nitrogen was detected confirming that processing cleanly removes both solvent and any amine based decomposition products of the DTC precursors. The low oxygen signal suggests the absence of significant oxidation of our AgBiS₂, even at high annealing temperatures. Analysis of the Ag 3d XPS data (Panel b) reveals binding energies of 367.8 eV and 373.8 eV for Ag 3d 5/2 and Ag 3d 3/2, respectively. Although the oxidation states of silver are somewhat troublesome to determine due to their small peak separation, the binding energies of the doublet match well to those previously observed for silver sulfide.⁴⁸ Furthermore, the line-shape of the silver peaks are highly symmetric and indicate a single component, with no loss features are observed in the range 371–372 eV as are typically seen in the presence of silver metal.^{49,50} Furthermore, the peaks have a FWHM of ~1 eV which is broader than that observed for metallic silver, and consistent with silver in an oxidized state.⁵¹ Similarly, the Bi 4f doublet was measured at 158.3 eV (Bi 4f7/2) and 163.6 eV (Bi 4f5/2) (Panel c). The measured positions are intermediate between those of bismuth metal (Bi 4f7/2, 157 eV) and bismuth oxides (Bi 4f7/2, 159 eV), which is expected and typical for bismuth sulfide.⁴⁸ Collectively, these data are indicative of silver and bismuth as a metal sulfides (Ag(I), Bi(III)), as consistent with previous data on AgBiS₂.^{37,35}

The two low intensity peaks (within the Bi 4f region) centered at 161.2 eV (S 2p3/2) and 162.3 eV (S 2p1/2) correspond to the S 2p doublet (Panel c). The binding energy of the S 2p3/2 is consistent with a metal sulfide environment and the coupling of spin orbit components

(1.14 eV) and their height ratio (0.511) is an excellent match to sulfur in the 2^- (sulfide) state.^{52,53,54} In order to determine the effect of temperature on the local crystal (bonding) environment we conducted XPS of the three main elements as a function of temperature. To obtain a clearer sulfur signal, data for the S 2s peak is also shown (225.3 eV). As shown in Panels d-f for (Ag 3d), (Bi 4f) and (S 2s) respectively, no appreciable differences in either peak position or shape as a function of annealing temperatures could be observed. As such, it may be concluded that annealing temperatures in the range (150 °C – 400 °C), while having an effect on grain size, has little effect on the nature of the chemical bonds (local atomic environment) of the elements constituting the AgBiS₂ semiconductor.

Figure 3. X-ray photoelectron spectra for stoichiometric AgBiS₂ film annealed at various temperatures. a) Survey spectra of a typical sample annealed at 300 °C. b) Ag 3d and c) Bi 4f regions for a typical AgBiS₂ film annealed at 300 °C showing the individual peak fittings. Panels d–f show the effects of annealing temperatures between 150–400 °C on the Ag 3d, Bi 4f (S 2p), and S 2s peaks respectively.

Fabrication of high quality ultra-thin films is of paramount importance for the use of silver bismuth sulfide in efficient optoelectronic devices. In fact, it has been demonstrated that solar cells incorporating AgBiS₂ as the absorber layer suffer from current losses when the absorber thickness is increased above ~50 nm.³⁵ Thus, it is advantageous to be able to obtain ultra-thin dense and pinhole films within this range. By depositing multilayers from a dilute metal DTC solution (0.075 M total metal concentration) we could achieve very accurate control of film thickness (down to ~10 nm per layer). The digital photographs shown in Figure 4a highlight the excellent macroscopic quality of 200 °C annealed thin films with between 1–7 layers. All AgBiS₂ films show absence of scattering and strong specular reflectance properties (*i.e.* smooth films), and are highly absorbing, despite their low thickness in the range ~30–80 nm.

To investigate the film morphology as a function of thickness SEM images were obtained for films with increasing layer number. Figure 4b–d show the SEM images of AgBiS₂ thin films with 1, 3, and 5 layers respectively. Increasing the number of layers results in larger more defined and faceted crystal grains. Notably, dense and uniform films are observed after three layers, which have an overall thickness of ~37 nm (Figure 4c). The coating obtained after a single deposition of dilute precursor solutions is not fully continuous. This is not surprising considering the extremely thin dimension of the coating, and the large volume loss occurring when decomposing the metal-DTC precursors into metal sulfides. However, the deposition of subsequent layers fills the gaps in the AgBiS₂ underlayer(s) and continuous, dense films are obtained after three layers. Figure 4e shows a plot of layer thickness as a function of the number of deposited layers. Due to incomplete coverage and densification of the thin films and variability in the wetting of the substrate thicknesses below three layers are non-linear with respect to layer number. For single layer films, the ITO substrate can be seen due to incomplete

coverage (see arrows in Figure 4b). However, it can be clearly seen that additional depositions (>3 layers) increase the overall thickness with almost perfect linearity (~ 10 nm per layer). As such, using the methods here dense and homogeneous ultra-thin AgBiS₂ films can be fabricated with thickness as low as 37 nm. Such ultra-thin films, as outlined here, are highly desirable and are on par with those thickness known to produce the highest efficiency AgBiS₂ solar cells.³⁵ We expect that the use of more dilute precursors (<0.075 M) can provide high quality films with even more reduced thicknesses.

Figure 4. Top view SEM images of AgBiS₂ thin films deposited from 0.075 M precursor solutions and annealed at 300 °C. a) 1 layer; b) 3 layers; c) 5 layers. The arrows in the single layer film (panel b) highlight the areas of incomplete coverage where the ITO underlayer is visible. All scale bars are 200 nm. d) Plot of thickness as a function of the number of deposited layers, showing a typical value of ~ 10 nm per layer.

Given the ultra-thin nature of the films and the rigorous requirements for (opto)electronic device incorporation, the quality of thin films is best assessed by viewing the films in cross sectional SEM. Figure 5 shows SEM images in cross-section for AgBiS₂ films (5 layers, 55–60 nm) on Glass/ITO substrates annealed at 150°C, 200 °C, and 300 °C. Dense, smooth and crystalline AgBiS₂ films can be seen for all temperatures, with a slight increase in

surface roughness at higher annealing temperatures, consistent with the larger crystal grain sizes obtained when annealing at 300 °C compared to lower temperatures. The corresponding top view SEM images are shown alongside each temperature. At 150 °C the film is seen to be highly uniform although the AgBiS₂ crystal grains are less faceted compared to those observed at 200 °C. Annealing at 300 °C causes the grains to become more faceted with well-defined grain boundaries. The data from Figure 5 (in conjunction with the previous XRD data) confirms that using the optimized methods outlined here dense highly crystalline thin films of AgBiS₂ can be obtained at processing temperatures as low as 150 °C. We attribute the ability to form high quality films at such low temperatures to the use of metal–DTC precursors, which are known to decompose at reduced temperatures compared to analogous metal thiourea complexes.^{55,56}

Figure 5. Cross sectional (left panels) and top view (right panels) SEM images of AgBiS₂ films deposited on ITO and annealed at 150 °C, 200 °C and 300 °C. Scale bars are 100 nm for cross sections and 200 nm for top views. Each sample has been fabricated depositing 5 layers (~55 nm) of a 0.075M DTC solution, annealing each layer directly at the desired temperature.

Having optimized the formation of dense thin films, the optical properties of the as-prepared AgBiS₂ films could then be confidently investigated. Figure 6 shows the results of a comprehensive study into optical properties of the films prepared at different annealing temperatures. The AgBiS₂ films were found to have an absorption onset at around 1200 nm (Figure S6). Figure 6a shows the results of extrapolating the optical band gap using Tauc analysis. A direct band gap value of ~ 1.1 eV is observed for all temperatures between 200–300 °C. The measured band gap was slightly larger for the lower annealing temperature of 150 °C (~ 1.15 eV). Further increases to the annealing temperatures resulted reductions to the band gap of less than 50 meV, with values of 1.06 eV (350 °C) and 1.05 eV (400 °C). From further analysis of the films we viewed an indirect component at ~ 0.9 eV (Figure S7), similar to recently reported data.³⁸ The dense, smooth and uniform nature of the thin films (with a precise thickness) enables accurate evaluation of the absorption coefficient, which is presented in Figure 6b. Remarkable values of $\alpha > 10^5 \text{ cm}^{-1}$ are achieved in the visible–NIR wavelength range (above 960 nm), putting AgBiS₂ on par with the best known semiconductor light absorbers (CdTe⁵⁷, CH₃NH₃PbI₃⁵⁸, GaAs⁵⁹ etc). Compared to recent works on AgBiS₂ thin films we achieved a slightly larger absorption coefficient.^{35,38} We ascribe this to the high density of the films prepared here, which are unlike previously reported AgBiS₂ films, especially those fabricated from colloidal nanocrystals, which incorporate a large fraction of pores.

We also evaluated the band structure of AgBiS₂ combining photoelectron spectroscopy in air (PESA) and valence-band XPS. PESA enables to measure the ionization potential of thin films, which corresponds to the valence band edge in a semiconductor (or the HOMO level in an organic material). This technique has been widely adopted to estimate valence band positions in various semiconducting materials including oxides and chalcogenides.^{60,22,61}

Analysis of the valence band (VB) region using XPS enables estimation of the energy difference between the Fermi level and the valence band edge. Figure 6c shows typical PESA and VB-XPS (inset) data collected for films annealed at 300 °C. The dotted lines show the linear fits used to determine the VB edge and the Fermi level offset. The spectra were then collected for a range of annealing temperatures. The PESA and valence band XPS spectra for AgBiS₂ samples annealed at different temperatures can be viewed in Figures S8 and S9. Using these data, in conjunction with the band gap energy (from Tauc analysis), simplified band structures can be drawn. From the band structures presented in Figure 6d we can conclude that AgBiS₂ is an almost intrinsic (slightly n-type) semiconductor, as the Fermi energy lies roughly in the middle of the band gap. Interestingly, we note that the films produced using DTC precursors are naturally more intrinsic than those of as-prepared AgBiS₂ nanocrystals, which are n-type and require ligand stripping and iodine doping to yield an intrinsic semiconductor.³⁵ Overall, annealing temperature was observed to have little effect on the band structure within the temperature range investigated here (see Figure 6d and Table S2 in Supporting information for details). In addition, phase-pure AgBiS₂ films with off-stoichiometric compositions - up to 40% excess of either metal (Ag:Bi = 1:1.4 – 1.4:1), see Figure 2 – showed small variations in band gap energy, without a clear trend with composition as presented in Figure S10. However, a weak trend in valence band energy could be identified using PESA, with the bismuth-rich samples having a slightly deeper valence band than the silver-rich samples (Figure S11). It is worth noting that the maximum variation both in band gap and valence band energies is within ~0.1 eV, therefore the effect is rather small.

Figure 6. a) dTauc plot assuming direct allowed transition for typical AgBiS_2 films annealed at different temperatures, showing a band gap value of about 1.1 eV. b) Absorption coefficient for a typical AgBiS_2 sample annealed at 300 °C as a function of radiation energy. The inset shows a digital photograph of a 60 nm thick film. c) Photoelectron yield as a function of energy of the incident radiation as measured with PESA for a typical AgBiS_2 sample annealed at 300 °C. The inset shows the valence band XPS spectrum for the same sample. d) Schematic band diagram for AgBiS_2 films as a function of annealing temperature.

In order to assess the potential performance of our AgBiS_2 films as light absorbers in photovoltaic devices, we conducted preliminary tests of their ability to generate photocurrent. AgBiS_2 films were deposited on lithographically patterned Au electrodes and exposed to pulsed green (530 nm) light using a commercial light emitting diode (LED). A fast and reversible photocurrent was observed in all samples tested, indicating the potential of the films for photovoltaic device integration. The tests were performed under inert gas environment which was observed to provide a more stable and reproducible baseline signal (dark current) compared to measurements performed in ambient air. Notably, the sample processed at 200 °C showed a drastic improvement in the on/off ratio (~ 2.2) compared to samples annealed at either higher (300 °C) or lower (150 °C) temperatures. The observed on/off ratios are similar to those

observed previously for photo-conductivity measurements employing lateral electrodes.^{38,62} From the data of Figure 7 it is clear that the photocurrent generation from AgBiS₂ thin films is extremely sensitive to the processing temperature used. The narrow temperature window to achieve optimal performance observed here is consistent with previous work on AgBiS₂, which showed drastic differences in both the optical properties and solar cell device performance (short circuit current) with very small changes to the processing temperature between 125–225 °C.³⁷ In fact, optimization of processing temperature to achieve maximum (thin film) device currents is commonly observed for semiconductors.^{63,64} Typically, higher processing temperatures result in improved grain growth and crystallinity and subsequent improvements to photocurrent. As such, the reduced photocurrent at 300 °C, although somewhat unexpected again highlights the critical importance on processing temperatures for this system. Elucidating the nature of the seemingly narrow processing temperature window for AgBiS₂ proves to be an interesting topic for further, more rigorous investigation. Finally, the high quality of our AgBiS₂ films is also evidenced through extended testing under chopped light (Figure S12), which shows excellent reproducibility and stability of both the dark current and photocurrent values.

Figure 7. Top panels: optical microscope images of the AgBiS₂ film deposited on pre-patterned Au electrodes. Bottom panel: Photoconductivity as a function of time for AgBiS₂ annealed at different temperatures under pulsed green (530 nm LED) light illumination.

CONCLUSION

Through careful optimization of the precursors and solvents we have developed a stable molecular precursor capable of fabricating pure phase ultra-thin (<40 nm) device quality AgBiS₂ films. Through mixing the precursor solution in the desired ratios, dense films of tunable composition with up to 40% excess of either metal can be achieved without the segregation of impurity phases. Detailed spectroscopic (optical, XPS, PESA) and structural (XRD, SEM) analyses confirm that highly crystalline AgBiS₂ films can be achieved at temperatures as low as 150 °C and up to 400 °C without compromising film quality or the materials electronic structure and phase purity. An optical band gap of ~1.1 eV and a striking

absorption coefficient $>10^5 \text{ cm}^{-1}$ in the visible range have been measured for our optimized films. Preliminary photocurrent measurements using lithographically patterned lateral electrodes under chopped visible (530 nm) light show a fast and reversible photo-response. Collectively, the low temperature processing conditions, high film quality, and the tunability of Ag/Bi composition make the AgBiS₂ thin films developed here highly desirable for optoelectronic applications and ideal for photovoltaic device integration.

EXPERIMENTAL

Materials

Silver acetate (99.99%), *n*-butylamine (99.5%), carbon disulfide (CS₂, >99.9%), pyridine (> 99.9%) were supplied by Sigma-Aldrich. Bismuth oxide (99.999%) was supplied by Strem Chemicals. All chemicals were used without further purification.

Precursor synthesis

All procedures reported below have been conducted in a fume hood. *n*-butyl dithiocarbamic acid (DTCA) was prepared by first reacting *n*-butylamine with CS₂. Specifically, 7.2 mmol (0.526 g) *n*-butylamine was mixed with 1.831 mL pyridine in a glass vial and let stir in an ice bath for 15 min. Then 7.56 mmol CS₂ (0.576 g, a 5% excess compared to the stoichiometric 1:1 amount with *n*-butylamine) was added dropwise under strong stirring. A color change from colorless to deep yellow was observed during the addition of CS₂. The solutions are let stir for an additional 5 minutes in the ice bath, and then are removed from the bath and let warm up naturally to room temperature under constant stirring.

This DTCA solution was used to dissolve either 0.6 mmol silver acetate (0.1001 g) or 0.3 mmol bismuth oxide (0.1398 g), in order to keep a 1:12 molar ratio between the metal and the DTCA (every bismuth oxide molecule contributes with two bismuth atoms), and a metal

concentration of 0.2 M for both Ag and Bi solutions. In the case of silver, some black precipitates form immediately after mixing, but they re-dissolve within 1 hr, forming a stable dark yellow solution of Ag-DTC complex.⁶⁵ Bismuth oxide requires a few days of constant stirring to fully dissolve into a deep red Bi-DTC complex. These equimolar solutions could then be mixed in 1:1 volume ratio to achieve stoichiometric AgBiS₂ precursors or mixed in the desired ratio for non-stoichiometric formulations. Notably, these molecular precursors are stable for several months if stored in an inert (oxygen and water free) environment. Moreover, these solutions could be further diluted with pyridine for the deposition of ultra-thin layers. Given pyridine contains an amine, pure pyridine solutions (without *n*-butylamine) were tested to evaluate the possible speciation of the precursor with the solvent. We note here that in the absence of *n*-butylamine no dissolution of the metal salts was observed, indicating that pyridine is unable to form a DTC complex with CS₂. This is expected given the greatly reduced reactivity (nucleophilicity) of secondary amines compared to primary amines.

Thin-film deposition

Thin films were deposited by spin coating on various substrates (glass, Si, glass/ITO or pre-patterned Si/SiO₂/Au samples, see below) which were pre-cleaned through washing in acetone and isopropanol. All depositions and annealing have been conducted in a nitrogen-filled glove box (H₂O/O₂ concentration < 10 ppm). Thick films for XRD analysis were prepared by spin coating 2 layers of a 0.2 M solution of metal precursors in the desired ratio at 3000 rpm for 30 seconds and annealed directly at the desired temperature on a preheated hotplate for 10 minutes. Drop-cast samples were prepared by preheating the substrate on a hotplate at the desired temperature, and by dropping the precursors solution slowly, giving time for the deposited material to decompose between additions.

Thin multilayered samples were prepared from 0.075 M precursor solutions, using 5000 rpm as the spin speed and annealing directly at the desired temperature for 2 minutes each layer. For samples annealed at 150 °C and 200 °C, longer baking times (10 and 5 minutes respectively) are needed for each layer to fully stabilize in order to avoid material delamination when depositing subsequent layers. All samples made in this study are stoichiometric (Ag:Bi =1:1) unless specified otherwise.

Characterization techniques

X-ray diffraction (XRD) patterns of thin films were collected using a Bruker D4 Endeavor diffractometer equipped with a Cu-K α radiation source and operated at 40 kV and 35 mA. The crystallite size was evaluated with the Scherrer relationship using the full width at half-maximum of the diffraction peaks fitted using Lorentzian functions. For each sample the extracted size values from each of the diffraction peaks were averaged and the error was calculated as one standard deviation. X-ray Photoelectron Spectroscopy (XPS) was conducted on a Thermo Scientific K-Alpha XPS equipped with a Monochromated Al K α X-ray source ($E_{\text{photon}} = 1486.7$ eV), X-ray spot size: 30-400 μm in 5 μm steps. Scanning electron microscopy (SEM) images were acquired on a FEI Verios 460L SEM operated at 2 kV and 25 pA. Thickness values were acquired with a KLA Tencor P-16+ Surface Profiler and validated with cross-sectional SEM images. Optical transmission (T) and reflection (R) spectra of AgBiS₂ films were acquired with a Cary 7000 UV-Vis-NIR spectrometer equipped with an integrating sphere. The absorption coefficient α was calculated from transmission and reflection data using the following formula:

$$\alpha = \frac{1}{d} \ln \left(\frac{1 - R}{T} \right)$$

where d is the AgBiS₂ thickness. Photoelectron spectroscopy in air (PESA) measurements were conducted on a Riken-Keiki spectrophotometer using an incident radiation power of 5 nW. The

electrical measurements as a function of light illumination were conducted on AgBiS₂ thin films deposited onto pre-patterned Au electrodes under a constant flow of nitrogen. The current under light and dark conditions was measured using a Keysight 2900 sourcemeter applying a constant voltage of 0.5 V. A green (530 nm) light-emitting diode (LED, Thorlabs, Inc.) was utilized as light source. The illumination power was calibrated using a silicon photodetector (Newport Corporation) and kept constant at 12 mW/cm².

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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