Thin film synthesis of SbSI micro-crystals for self-powered photodetectors with rapid time response†

Karl C. Gödel and Ullrich Steiner*

We describe a new thin film deposition method for the growth of crystalline SbSI micro-needles via the conversion of Sb2S3 using SbI3 vapour, in a facile process that takes less than 15 minutes. These films were used to construct photodetectors in a sandwich-type architecture, which are superior to previously reported SbSI photodetectors. The devices exhibit a detectivity of $D^* = 10^9$ Jones, a signal-to-noise ratio greater than $SNR = 10^3$ and a responsivity of $R = 10^{-5}$ AW$^{-1}$. In time response measurements, rise and fall times of less than 8 ms and 34 ms were determined. This manufacturing method greatly simplifies the creation of fast photodetectors.

1 Introduction

Photodetectors are optoelectronic devices designed to convert light into electrical signals. They play an important role in a wide range of applications, from alarm systems and smoke detectors to consumer electronics and optocouplers for electronic circuits. Most commercial photodetectors use semiconducting materials such as Si, InGaAs, GaN or CdS. Recent research focuses however on new materials with facile deposition methods for inexpensive and scalable light sensing devices. In particular, quantum dots, polymer blends and organo-metal perovskites were investigated for photodetector applications.1,2

The photoconductive properties of antimony sulfoiodide (SbSI) are long known.3-6 First photoconductivity measurements using antimony sulfoiodide nanowires were presented by Nowak et al. in 2013,7 which were subsequently employed for humidity sensing applications.8 In 2015, Chen et al. demonstrated a SbSI photodetector based on a macroscopic single crystal.9

Antimony sulfoiodide exhibits a series of interesting properties. It is a ferroelectric material with a Curie temperature of $T_C = 22 \, ^\circ$C, a high piezoelectric constant and pyroelectric properties.10 The n-type semiconductor has an indirect band-gap of $E_g = 1.8-1.9$ eV.11,12 Theoretical calculations suggest a high charge mobility of antimony sulfoiodide caused by low effective masses of the charge carriers, making it a promising material for photovoltaic applications.12

Here, we present a novel synthesis method for SbSI micro-crystals in a thin-film deposition route. We use this method to fabricate a SbSI photodetector with a sandwich-type architecture. This significantly improves the photodetector figures-of-merit, compared to earlier devices.9

2 Results and discussion

2.1 A new method for the synthesis of SbSI micro-crystals

Several synthesis routes for antimony sulfoiodide (SbSI) have been proposed in literature. Most common are a sonochemical method from elemental antimony, sulfur and iodine,8,13 hydrothermal deposition in an auto-clave14 or chemical vapour deposition at high temperatures.15 These methods have long processing times of 4 h and more9,15 and result in bulk SbSI crystals.

Here, we report on a new two-step synthesis method, where SbSI micro-crystals are formed in a thin film. The first step entails the deposition of a thin film of antimony sulfide (Sb2S3) in a low temperature chemical bath as previously described.16,17 The second step is the conversion of the amorphous Sb2S3 to crystalline SbSI using antimony iodide vapour (SbI3). This chemical reaction was described before as part of a hydrothermal deposition method14

$$\text{Sb}_2\text{S}_3 + \text{SbI}_3 \rightarrow 3\text{SbSI}.$$ (1)

To prevent oxidation of the antimony sulfide, the conversion reaction has to take place in an inert N2 atmosphere.
First, a SbI₃ evaporation target was prepared by the dissolution of SbI₃ crystals and drop-casting of the solution on a microscope slide. The substrate with pre-deposited Sb₂S₃ was mounted facing the antimony iodide target as shown in Fig. S2.† The target was heated to \( T_t = 250 \, ^\circ \text{C} \) within 5 min. The temperature \( T_t \) of the SbI₃ target and \( T_s \) of the substrate were recorded using a Pt100 temperature sensor (Fig. S3†).

Within less than 5 min, an excess of antimony iodide sublimes and reacts with the Sb₂S₃ on the substrate to form SbSI. This reaction is indicated by a colour change of the sample from bright orange to dark red. To increase the crystallinity, the SbSI sample was heated for another 10 min. After cooling, the samples were rinsed in ethanol to remove residual SbI₃.

To confirm the formation of crystalline SbSI, the films were characterised by X-ray diffraction (XRD) and UV-vis spectroscopy. As schematically shown in Fig. 1a, antimony sulfoiodide has an orthorhombic crystal lattice, consisting of long chains along the (001)-axis. This anisotropy leads to the preferential growth of SbSI into needle like crystals. Fig. 1b shows the XRD pattern of SbSI films as-deposited on a fluorine doped tin oxide (FTO) covered glass substrate. The peaks are in good agreement with the reference pattern for antimony sulfoiodide (JCPDS-ICCD PDF 00-021-0050). Additional peaks can be attributed to tin oxide (JCPDS-ICCD PDF 00-046-1088) originating from the FTO layer of the substrate. The absence of other peaks, in particular those of Sb₂S₃, indicates the formation of pure crystalline SbSI. The intensive scattering peak between 18°–35° is caused by the FTO-glass substrate as confirmed by a reference measurement (Fig. S4†).

The band-gap of SbSI was reported to lie at \( E_g = 1.9 \, \text{eV} \). The onset for the absorption should therefore be at a wavelength of \( \lambda_g = \frac{hc}{E_g} \approx 650 \, \text{nm} \). The transmittance onset of the UV-vis spectrum in Fig. 2a is in good agreement with this value. Due to the micro-structure of the SbSI film, the samples exhibit strong light scattering and the diffuse transmittance spectrum had therefore to be recorded using an integrating sphere. The inset in Fig. 2a shows the typical red colour of the SbSI samples. A comparison to the amorphous Sb₂S₃ sample before the conversion process with SbI₃ is shown in Fig. S1†.

The microscopic structure was further investigated using scanning electron microscopy (SEM). Fig. 2b confirms the needle like morphology of SbSI crystals. The length of the individual crystals lies between 1–5 μm. The width of the needles is on the order of 10–100 nm. Cross-sectional SEM images (Fig. S6†) suggest a preferred orientation: the needles grow preferentially perpendicular to the surface, which might be induced by the roughness of the underlying FTO substrate. Note that the initial Sb₂S₃ film is flat (Fig. S5†).

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**Fig. 1** (a) Schematic crystal structure of SbSI, showing long chains along the (001)-axis, which causes the preferential growth into crystal needles. (b) XRD pattern of as-prepared SbSI samples in comparison with reference patterns for SbSI and SnO₂.

**Fig. 2** (a) Transmittance spectrum of a SbSI film on a quartz substrate measured using an integrating sphere. The inset shows a photograph of the SbSI sample. (b) Top view scanning electron microscopy (SEM) image of as-prepared SbSI micro-crystals.
2.2 Fabrication of SbSI photodetectors with a sandwich-type architecture

Our new SbSI micro-crystal deposition method was used to fabricate functional optoelectronic devices. Earlier approaches to harness the photoconductive properties of SbSI in humidity-sensors and photodetectors were based on devices with macroscopic electrode spacings (0.1–1 mm). These large spacings limit both, the maximum photocurrent signal and the time response of the detector. We have instead fabricated photodetectors with a sandwich-type architecture by contacting the SbSI crystals with an electrode spacing of less than 2 μm.

The fabrication process of the device is schematically shown in Fig. 3a. The first two steps (Step 1 and 2) show the deposition of antimony sulfide and the conversion to SbSI micro-crystals by SbI₃, as described above. Then, an insulating buffer layer was deposited by spin-coating of poly(methyl methacrylate) (PMMA) from chlorobenzene with a concentration of 100 mg ml⁻¹ (Step 3). Process optimisation revealed that one layer of PMMA is often not sufficient to prevent shorting between the top and the bottom electrodes, thus two layers were spun-on subsequently. This PMMA layer entirely covered the SbSI crystals, preventing electrical contact with the top electrode. To partly etch the PMMA layer to reveal the tips of the crystals, pure chlorobenzene was dynamically spin-coated (Step 4). Finally, a gold metal electrode was deposited by electron beam evaporation (Step 5). A cross sectional SEM image of the final photodetector is shown in Fig. 3b. For clarity, a sketch of the device is shown in Fig. 3c. This schematic illustrates the working principle of the photodetector. Photons with energies higher than the band-gap of SbSI are absorbed by the detector, generating charge carrier pairs. These are preferentially transported along the (001) axis of the crystal needles, driven by an external applied electric field (generated by a bias voltage V_b). The density of free charge carriers is dependent on the intensity of the incident light, resulting in a variable photocurrent as electrical output signal.

2.3 Characterization of SbSI photodetectors

Fig. 4a shows the current–voltage characteristics of the photodetector in the dark (blue squares) and under white light illumination of a solar simulator with an irradiance of E_e = 100 mW cm⁻² (yellow circles). Each voltage step was followed by a 30 s stabilisation period. Note that the photodetector has a photocurrent of approx. I = 40 nA even under zero bias V_b = 0 V. This probably arises from the use of two different electrode materials, namely FTO on the bottom and gold on the top. The two electrodes have different work functions, causing a built-in potential. To further investigate this, symmetric photodetectors with an additional thin gold-layer on top of the FTO electrode were fabricated. In these devices, the short circuit current under zero bias was considerably reduced, by approximately one order of magnitude (Fig. S10†).

The asymmetric device is thus be self-powered and can be used without an externally applied voltage. Fig. 7 in the ESI† shows the spectral response and the irradiance dependence of the SbSI photodetector at V_b = 0 V. Signal-to-noise ratio, detec-

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**Fig. 3** (a) SbSI photodetector fabrication process in 5 steps. (b) Cross sectional SEM micrograph of a SbSI photodetector. (c) Illustration of the working principle of the photodetector. The illumination direction is from the bottom.
where $f$ is the electrical frequency bandwidth of the detector. Assuming that the noise current $I_n$ is dominated by the shot noise of the dark current $I_{dark}$, the specific detectivity can be written as

$$D^* = \frac{\sqrt{A R}}{2e I_{dark}}$$

where $e$ is the elementary charge. The specific detectivity $D^*$ is measured in Jones ($1 \text{ Jones} = 1 \text{ cm} \text{ W}^{-1} \text{ s}^{-0.5}$). For the photodetector described here, the specific detectivity is on the order of $D^* = 10^9$ Jones for a bias voltage of $V_b = 100$ mV, plotted as a function of $E_e$ in Fig. 4c (bottom).

Compared to previously published SbSI photodetectors, the figures-of-merit of our devices are significantly improved. The maximum signal-to-noise ratio is nearly doubled and the specific detectivity is enhanced by a factor of three compared to the best previous device. The figures-of-merit in self-powered mode without applied bias voltage ($V_b = 0$ V) are on the same order of magnitude (Fig. S8†).

For many optical sensing applications, short response times to changing light signals are essential. We used an array of white light LEDs pulsed by a function generator with a rectangular waveform and measured the current response of the SbSI devices using an Autolab potentiostat in fast chronamperometry mode with a bias voltage of $V_b = 100$ mV.

Fig. 5a shows the photocurrent response to a modulated light signal with a frequency of $f = 2$ Hz with a peak intensity of $E_e = 80$ mW cm$^{-2}$. A detailed view of one modulation cycle is shown in Fig. 5b. The rise (fall) time $\tau_r$ ($\tau_f$) is the current increase (decrease) from 10% (90%) to 90% (10%) of the maximum signal. Averaged over ten modulation cycles, values of $\tau_f = 7.4 \pm 0.4$ ms and $\tau_r = 33.8 \pm 1.5$ ms were determined, where the errors are the standard deviations. $\tau_r$ is two orders of magnitudes and $\tau_f$ one order of magnitude faster compared to previously reported SbSI photodetectors.

The time response of a photoconductive light sensor under bias is dominated by the drift time of the charge carriers and the RC constant of the device. The significant improvement in time response of our photodetector can be explained by its sandwich-type architecture. The short electrode distance of

Fig. 4  (a) $I$–$V$-characteristic of the SbSI photodetector. (b) Photocurrent $I_{light}$ as a function of the illumination irradiance $E_e$. (c) Signal-to-noise ratio SNR, responsivity $R$ and specific detectivity $D^*$ as a function of $E_e$ at a bias voltage of $V_b = 100$ mV.
1–2 μm leads to a high electric field $E$ at a given bias voltage. As the drift velocity $v_d$ of charge carriers increases with the electric field ($v_d = -\mu E$, where $\mu$ is the charge carrier mobility), the time response of our photodetector benefits from the small thickness of its active layer. As the active area $A = 0.12 \text{ cm}^2$ is relatively large for a light sensor, the time constants could be even further improved by reducing the area and hence the RC constant. This would however also lead to a decrease of the current output. Higher bias voltages $V_b$ can also further improve fall- and rise-times, but at the cost of an increased noise current and hence a decreased signal-to-noise ratio SNR.

Fig. 5c shows the spectral response of the photodetector at a bias voltage of $V_b = 100 \text{ mV}$, by plotting the measured photocurrent as a function of wavelength, normalised by the light intensity. A tungsten halogen lamp, a grating monochromator and a calibrated photodiode were used for this measurement. The output current has a clear onset at $\lambda = 650 \text{ nm}$, which corresponds well to the reported band-gap energy for antimony sulfide $E_g = 1.9 \text{ eV}$ (ref. 12) and further agrees with the UV-vis spectrum in Fig. 2a. It shows that the detector is sensitive to most of the visible spectrum from red to blue. The spectral response at zero bias is shown in the ESI (Fig. S7†).

3 Conclusion

We introduce a new method for the deposition of SbSI needle-shaped micro-crystals via the evaporation of SbI$_3$ onto amorphous Sb$_2$S$_3$. The conversion process is facile and fast, with complete conversion in under 15 min. SbSI covered substrates were employed in the fabrication of sandwich-type photodetectors. Optoelectronic investigations showed remarkable improvements compared to previously published SbSI light sensors. In particular, the response and recovery time of these photodetectors is improved by one to two orders of magnitude. A promising specific detectivity of more than $D^* = 10^8$ Jones, a responsivity $R = 10^{-5} \text{ A W}^{-1}$ and a high signal-to-noise ratio of more than $\text{SNR} = 10^3$ show that SbSI sandwich architectures are promising for the manufacture of efficient and low-cost light detectors. This is further substantiated in Table S1† where SbSI photodetectors, a perovskite and a high performance CdSe-nanowire photodetector are compared.

4 Experimental section

4.1 Photodetector fabrication

The sample preparation steps are illustrated in Fig. 3a. All chemicals were purchased from Sigma-Aldrich and used without further purification. The FTO substrate ($15 \Omega \text{ cm}^{-1}$) was cleaned by sonication in acetone and ethanol and then partly etched using a 2 M solution of HCl and zinc powder to prevent shorting during the measurements. Amorphous Sb$_2$S$_3$ was deposited in a low-temperature aqueous chemical bath as described elsewhere. Anhydrous SbI$_3$ crystals were dissolved in anhydrous ethanol at a concentration of 1 mg ml$^{-1}$. 2 ml of the solution were spread on a microscope slide at 100 °C to evaporate the ethanol. This way, a thin, uniform layer of SbI$_3$ was formed, which was used as target for evaporation.

The target was placed onto a hotplate (Stuart CD162) in an inert atmosphere and covered by a 15 mm high petri-dish (see Fig. S2†). The Sb$_2$S$_3$-covered FTO sample was fixed to the bottom of this petri-dish, facing the SbI$_3$ target. The temperature of the hotplate was ramped to 250 °C within 5 min and held at this temperature for 10 min. The evaporation of SbI$_3$ was observable by the condensation on the petri-dish. Within the first 5 min, the colour of the sample changed from orange to dark red, indicating the formation of SbSI crystals.

The samples were left to cool under inert atmosphere. They were then rinsed in absolute ethanol to remove excess SbI$_3$. A PMMA film was applied onto the SbSI-covered substrate by spin-coating of a 100 mg ml$^{-1}$ PMMA solution in chlorobenzene (Laurell Spin Coater Model WS-650MZ-23NPP). To increase the thickness of the polymer film, two layers were spin-coated subsequently at 4000 rpm. As a third step, pure chlorobenzene was dynamically spin-coated to remove the top layer of
4.2 Material characterisation

Optical transmission measurements were carried out using a solar simulator from ABET Technologies (Model 11016 Sun 2000) with a xenon arc lamp and recorded using a Keithley 2635 sourcemeter controlled by a Python program. The intensity of the solar simulator was calibrated to 100 mW cm\(^{-2}\) using a silicon reference cell from Czibula & Grundmann (FHG-ISE, RS-OD4). To alter the irradiance, neutral density filters from Thorlabs (NEK01S) were employed.

The spectral response measurements were carried out using a 250 W tungsten halogen lamp and an Oriel Cornerstone 130 monochromator. The photocurrent was measured by a Keithley 2635 sourcemeter controlled by a Python program. The light was modulated by a Hewlett Packard 33120A function generator and the response of the photodetector was measured with a xenon arc lamp and recorded using a Keithley 2635 sourcemeter controlled by a Python program. The intensity of the solar simulator was calibrated to 100 mW cm\(^{-2}\) using a silicon reference cell from Czibula & Grundmann (FHG-ISE, RS-OD4). To alter the irradiance, neutral density filters from Thorlabs (NEK01S) were employed.

4.3 Optoelectronic measurements

Current–voltage characteristics were measured under a solar simulator from ABET Technologies (Model 11016 Sun 2000) with a xenon arc lamp and recorded using a Keithley 2635 sourcemeter controlled by a Python program. The intensity of the solar simulator was calibrated to 100 mW cm\(^{-2}\) using a silicon reference cell from Czibula & Grundmann (FHG-ISE, RS-OD4). To alter the irradiance, neutral density filters from Thorlabs (NEK01S) were employed.

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