Growth of Highly Oriented Chalcocite Thin Films on Glass by Aerosol-Assisted Spray Pyrolysis Using a New *Single-Source* Copper Thiolate Precursor

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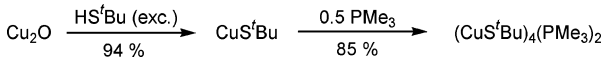
The development of Cu_xS thin films for photovoltaics slowed in the late 1980s because of the intrinsic instability of CdS/Cu_2S heterojunction cells.[1] However, *n*-type semiconductors such as TiO_2 and ZnO have recently been shown to yield stable *p*/*n* heterojunction cells with cuprous sulfide, stimulating renewed interest in high-quality Cu_xS films.[2,3] Among the Cu_xS phases exhibiting photovoltaic activity, monoclinic chalcocite[4] has the smallest band gap and conductivity.[5] Because the topotactic ion exchange, typically used for high-quality CdS/Cu_2S heterojunctions, is not possible for producing Cu_2S/metal−oxide heterostructures, gas-phase deposition techniques are attractive for the growth of high-quality Cu_2S thin films. Currently radio frequency (RF) sputtering of copper targets in a H_2S atmosphere[6] and low-pressure physical vapor deposition[7] are the only available gas-phase methods for growing phase-pure α-Cu_2S thin films.[8] Although the *single-source* precursor approach is very efficient for metal chalcogenide deposition by chemical vapor deposition,[9] no *single-source* precursors currently exist for α-Cu_2S.[10] However, in situ generated Cu(I) thiolates and mixed metal thiolate *single-source* precursors have been employed for hexagonal chalcocite nanoparticles[11] and $CuES_2$ (E = Ga, In) chalcopyrite powders and thin films,[12] respectively. These results raise the intriguing question of whether copper(I) thiolates could be effective precursors for growth of copper-rich chalcocite thin films. We report here on the synthesis of a new, highly soluble copper(I) thiolate *single-source* precursor and its implementation in the growth of high-quality α-Cu_2S thin films by aerosol-assisted spray pyrolysis.

Scheme 1



Light-sensitive CuS^tBu (**1**) was synthesized in high yield (Scheme 1) by a modified literature procedure (Supporting Information).[13] CI-MS of **1** up to $m/z = 800$ shows tetrameric $[CuS^tBu]_4$ as the heaviest and major gas-phase species, a common cluster size for copper(I) thiolates in the solid state.[14] Atmospheric pressure thermogravimetric analysis (TGA) of **1** (Figure 1)[15] shows a relatively narrow thermal decomposition range (170−225 °C) with a residue of 52.0%, which is in excellent agreement with that calculated for decomposition to Cu_2S (52.1%). The calculated decomposition onset and point of maximum rate of weight loss (PMRW) are 198 and 215 °C (at 48 mass % decomposition), respectively. TGA at 0.8 Torr leaves a residue of ∼8 mass % with sublimation onset (169 °C) and PMRW (187 °C, 93 mass % loss) approaching the decomposition values at atmospheric pressure. Therefore, complex **1** sublimation is accompanied by significant decomposition, and attempts to employ **1** as precursor in conventional low-pressure metal-organic CVD (LP-MOCVD) were unsuccessful, because of premature decomposition and sintering in the precursor reservoir.

Reaction of **1** with 0.5 equiv PMe_3 in diethyl ether affords moderately air-sensitive $(CuS^tBu)_4(PMe_3)_2$ (**2**) in >80% yield (Scheme 1; Supporting Information). Complex **2** is stable

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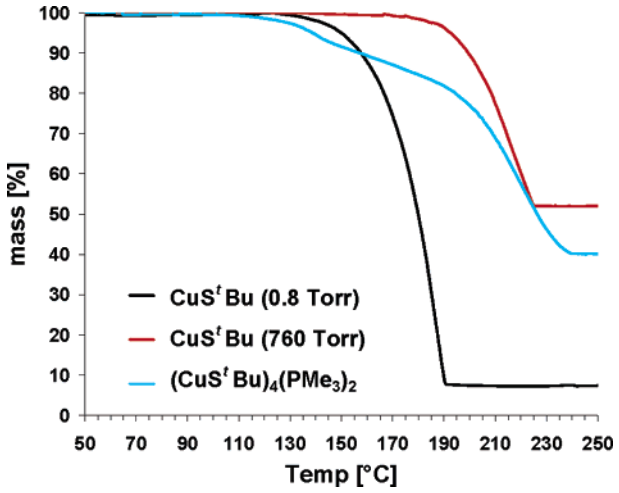

Figure 1. TGA traces of CuS^{t}Bu (**1**) under N_2 at 0.8 Torr (black line) and at atmospheric pressure (red line) and $(CuS^tBu)_4(PMe_3)_2$ (**2**) at atmospheric pressure (blue line).

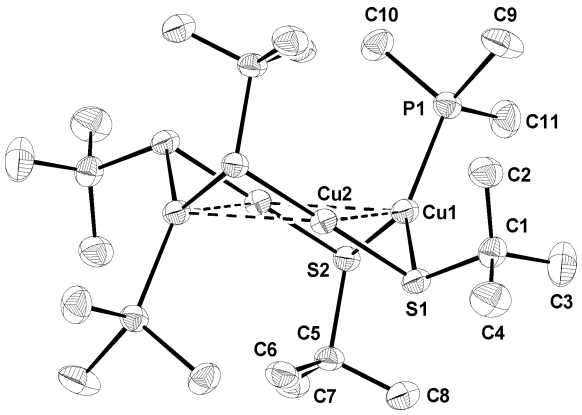

Figure 2. Solid-state molecular structure of $(CuS^tBu)_4(PMe_3)_2$ (**2**) with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Unlabeled atoms are related to the labeled ones via the crystallographic inversion center in the middle of the Cu_4 quadrangle. Selected distances (Å) and angles (deg): Cu1−Cu2, 2.8733(7); Cu1−Cu2A, 2.9483(9); Cu1−S1, 2.2331(9); Cu1−S2, 2.2970(9); Cu2−S2, 2.1603(9); Cu2−S1A, 2.1629(9); Cu1−P1, 2.2381(9); Cu2−Cu1−Cu2A, 77.55(2); Cu1−Cu2−Cu1A, 102.454(19); S1−Cu1−P1, 138.25(3); S2−Cu1−P1, 103.07(4); S1−Cu1−S2, 118.09(3); and S1A-Cu2−S2, 173.57(4).

in toluene as assessed by NMR for more than 2 weeks under N_2 but slowly decomposes upon exposure to light. Single-crystal X-ray diffraction (XRD) of **2** reveals a tetrameric cluster in the solid state (Figure 2; Supporting Information) similar to that of $(CuS^tBu)_4(PPh_3)_2$.[16] Full structural details will be discussed elsewhere.[17] Electrospray mass-spectrometry of CH_2Cl_2 solutions shows a cluster series $[Cu_{x+1}(S^tBu)_x(PMe_3)_y]^+$ having $x \geq 4$ with the maximum size around $x = 9$[18] and no ligand chemical degradation. Therefore, aerosol-assisted spray pyrolysis should be an ideally mild delivery technique for film growth with **2,** avoiding premature precursor decomposition. TGA analysis of **2** at atmospheric pressure (Figure 1) reveals stepwise decomposition between 105 and 240 °C, leaving a residue

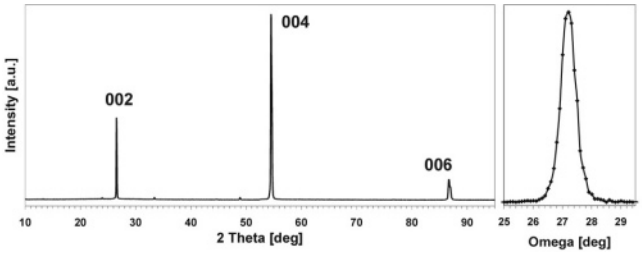

Figure 3. Left side: $\theta-2\theta$ XRD pattern of a 320 nm chalcocite film deposited from a toluene solution of **2** on glass at 270 °C (Cu Kα, 1.541 Å). The 00*l* peak assignment refers to the hexagonal sublattice of β-Cu_2S (JCPDS 26-1116). Right side: ω-scan rocking curve of the film 004 peak.

(40.1 mass %) very close to that calculated for clean decomposition to Cu_2S (41.7%). A first step (residue, ∼90%; calculated onset, ∼130 °C) is tentatively assigned to initial PMe_3 loss ([$(CuS^tBu)_4PMe_3$], 90.0%). The shallow TGA trace leads to a rise in slope at around 200 °C/∼78 mass % with the curve evolution suggesting further phosphine loss to give CuS^{t}Bu (80.1 mass %), which is complete in the range of CuS^{t}Bu decomposition onset. Therefore, **2** is an amply soluble CuS^{t}Bu (**1**) source in apolar solvents and undergoes, like **1**, clean thermal decomposition to Cu_2S.

The applicability of **2** as a *single-source* Cu_2S precursor was demonstrated using aerosol-assisted spray pyrolysis of toluene solutions (Supporting Information). Smooth, brown, 190−320 nm thin films, strongly adherent by the "Scotch tape test", were grown on glass substrates at 270 °C at rates of ∼1.5 nm/min. $\theta-2\theta$ XRD scans of the films (Figure 3) can be indexed in the hexagonal β-Cu_2S lattice (*high*-chalcocite, JCPDS 26-1116) with a high preferential 00*l* orientation as observed for reactively RF-sputtered Cu_2S films.[6] The ω-scan rocking curve of the 004 peak (fwhm = 0.6°) further documents the extremely high out-of-plane orientation of the films on an amorphous substrate. However, β-Cu_2S films undergo reversible phase transitions around 80 °C to monoclinic *low*-chalcocite Cu_xS ($1.997 \leq x \leq 2.000$) or *pseudo*-orthorhombic djurleite ($1.942 \leq x \leq 1.988$) phases,[19] both representing superstructures with only marginal distortions of the hexagonal β-Cu_2S anion sublattice.[20] Therefore, 00*l* ordered β-Cu_2S films are not easily distinguished from α-Cu_2S or djurleite by $\theta-2\theta$ scans. In the present work, XRD of the powder detached from the substrate by ultrasonication identifies the material as monoclinic α-Cu_2S (JCPDS 33-0490).[21]

A scanning electron microscopic (SEM) image of a typical film reveals large plates with in-plane dimensions in the ∼1−2 μm range (Figure 4). Note that the grain boundaries are oriented parallel to the substrate normal, separating hexagonally-shaped microplatelets. Both the crystallographic orientation and the film microstructure, therefore, suggest an island growth mechanism. The root-mean-square (rms) roughness by atomic force microscopy of single grains is as low as 1−3 nm over an area of 1−2 μm^2, in accord with

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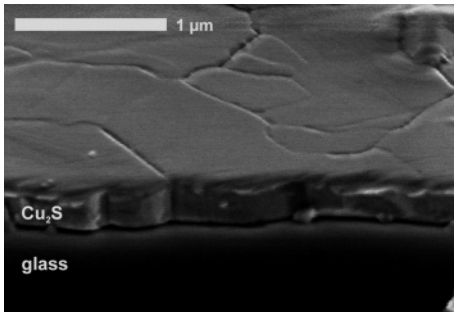

Figure 4. Cross-sectional SEM image of a 320 nm chalcocite film on glass.

highly uniform growth. The rms film roughness over 25 μm^2 is ~10 nm.

No features of C, O, or P impurities are detected in the Cu_2S films by X-ray photoelectron spectroscopy after cleaning the surface by brief Ar^+ sputtering (15 min/~45 Å). All Cu peaks are free of satellites, implying the absence of Cu^{II}.[22] The binding energies of the Cu $2p_{3/2}$ and $2p_{1/2}$ (932.8 eV, 953.1 eV) and S 2p features (161.8 eV) are in agreement with those of bulk Cu_2S.[23] Electrical properties were characterized by four-probe and Hall-effect measurements at room temperature. Conductivities, Hall mobilities, and hole concentrations are in the range of 16−32 S/cm, 3.2−4.2 $cm^2/(V\ s)$, and $2.3-6.2 \times 10^{19}\ cm^{-3}$, respectively. Heavy p-type doping was similarly observed in RF-sputtered α-Cu_2S films.[6c,24] The hole concentration in chalcocite is linearly related to copper vacancies at the valence band edge which act as acceptors with high ionization probabilities.[24b] This suggests our films to be in the compositional range $Cu_{1.999}S$−$Cu_{1.997}S$. Indirect (1.4 eV) and direct (2.2 eV) band gaps of a 320 nm film were estimated by transmission optical spectroscopy from $(\alpha h\nu)^{1/2}$ vs $h\nu$ and $(\alpha h\nu)^2$ vs $h\nu$ plots and agree well with the band gaps of α-Cu_2S single crystals along the same crystallographic axis.[25]

In conclusion, we presented the synthesis, characterization, and thermal stability characteristics of phosphine complex **2** as a soluble source of polymeric **1**. The efficacy as the first *single-source* precursor for deposition of α-Cu_2S was demonstrated by aerosol-assisted spray pyrolysis growth of phase-pure,[21] highly textured chalcocite thin films on glass. The good organic solvent solubility suggests further utility of **2**, for example, for the preparation of cuprous sulfide nanoparticles or Cu_2S/polymer hybrid structures. These results support a general applicability of phosphine-stabilized copper(I) thiolates as a new class of *single-source* Cu_2S precursors.

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Supporting Information Available: Synthetic schemes and analytical data for **1** and **2**, X-ray structural information on **2**, and film growth and characterization details (PDF). X-ray crystallographic file of **2** (CIF). This material is available fee of charge via the Internet at http://pubs.acs.org.

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