Communications

Solution-Processed Metal Chalcogenide Films for p-Type Transistors

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Solution-processed thin-film semiconductors may offer a route to low-cost and flexible thin-film transistors (TFTs) with performance sufficient for applications such as large area displays, wearable computers, radio frequency identification tags, and paperlike displays.[1-3] Transistors incorporating soluble organic and polymeric semiconducting thin films have been demonstrated with field-effect hole mobilities of up to ~1 cm²/(V·s),[4,5] comparable to amorphous silicon TFTs, and lower electron mobilities on the order of 10^{-2} cm²/(V·s).[6-9] Likewise, hybrid organic—inorganic materials maintain the processibility of organic semiconductors while carrying current in an inorganic network to achieve hole mobilities of ~1 cm²/(V·s).[10,11] More recently, solution-processed inorganic semiconductors, based on nanomaterials[12,13] or molecular precursors,[14,15] have emerged as an alternative capable of even higher performance. Metal chalcogenide TFTs have been fabricated using low temperature ($T \leq 350$ °C) solution processing, exhibiting electron mobilities in the range of $10-20$ cm²/(V·s).[14,15] High performance amorphous oxide flexible transistors have also recently been produced at room temperature by pulsed laser deposition, retaining some benefits of solution processing and yielding electron mobilities of $6-9$ cm²/(V·s).[16] These results expand the range of potential applications for flexible and/or solution-processed transistors by approaching the performance of polycrystalline silicon. However, analogous p-type devices, required for complementary logic or p—n heterojunctions, have not been demonstrated to date. We report the first p-type TFTs with spin-cast all-inorganic channels. The hydrazine-precursor method used previously for binary n-type compounds[14,15] is modified and extended to prepare thin films of the ternary (bimetallic) compound copper indium diselenide ($CuInSe_2$). As $CuInSe_2$ is also a candidate for application in photovoltaic cells, alternative

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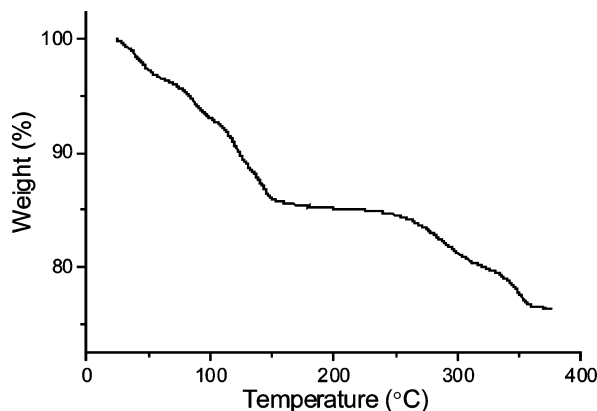(16) Nomura, K.; Ohta, H.; Takagi, A.; Kamiya, T.; Hirano, M.; Hosono, H. *Nature* **2004**, *432*, 488−492.

Figure 1. Thermogravimetric analysis of $(N_2H_4)_x(N_2H_5)_3(In_2Cu_2Se_4S_3)$, $x \approx 0.7$ powder. The multistep conversion to $CuInSe_2$ occurs as the precursor is heated at 2 °C/min in flowing nitrogen. Weight loss begins at room temperature and proceeds through a series of steps with maximal rates of weight loss at approximately 45, 90, 120, 145, 285, and 350 °C. The lower temperature transitions (below 200 °C) are consistent with the loss of hydrazine and related species, with the amount of weight lost in the first transition consistent with the neutral hydrazine content of the proposed precursor composition. The final transitions, above 250 °C, are consistent with the loss of excess chalcogen.

preparation strategies for relatively thick films of this material have been investigated, including recent advances in spray chemical vapor phase deposition[17-19] and in direct electrochemical deposition.[20,21]

A soluble precursor was prepared[22] by combining a copper(I) sulfide (Cu_2S) and sulfur (1:2 molar ratio) solution with an indium(III) selenide (In_2Se_3) and selenium (1:1) solution, each prepared in freshly distilled hydrazine using a process similar to that described previously for binary main group metal chalcogenides.[14,15,23] Alternatively, Cu_2S, In_2Se_3, sulfur, and selenium (1:1:2:1) can be dissolved together in a single reaction. *Caution: hydrazine is highly toxic and should be handled carefully for protection from both the liquid and the vapor.* The solvent was removed under flowing nitrogen to leave a dark powder, which is amorphous by X-ray diffraction. The multistep thermal decomposition of the precursor material (Figure 1) begins near room temper-
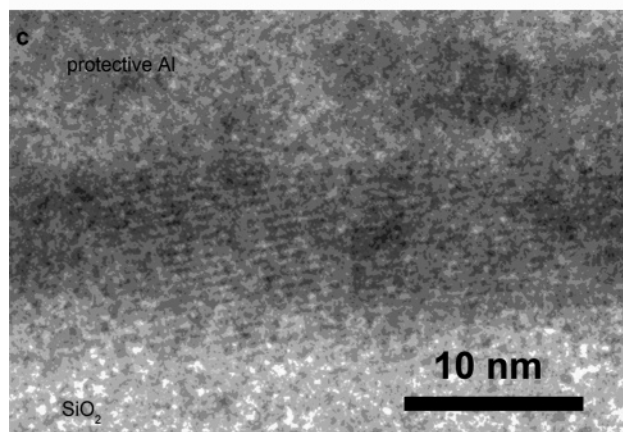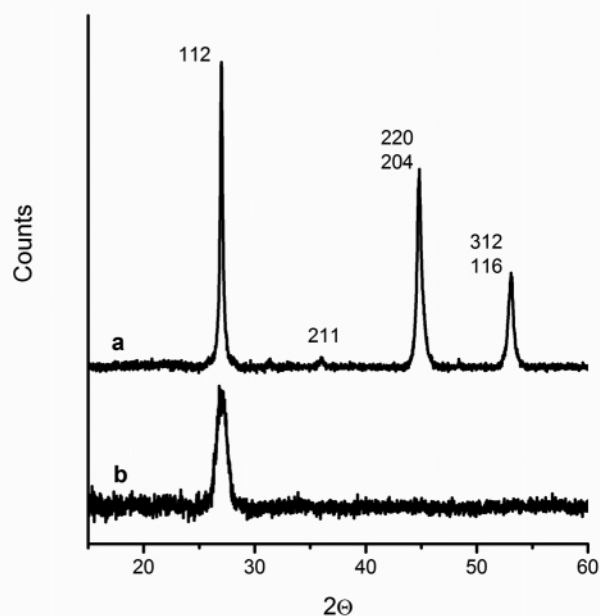
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(22) A Cu_2S solution was prepared by dissolving 159 mg (1 mmol) of Cu_2S and 64 mg (2 mmol) of S in 4 mL of distilled hydrazine to form a clear yellow solution. An In_2Se_3 solution was prepared by dissolving 467 mg (1 mmol) of In_2Se_3 and 79 mg (1 mmol) of Se in 4 mL of distilled hydrazine to form a clear, viscous solution. The two solutions were mixed in equal proportions, and the hydrazine was removed under flowing nitrogen. Two milliliters of the final solution yielded 163 mg of the dark colored precursor powder. Chemical analysis (performed by Galbraith Laboratories) observed N (11.5%) and H (2.0%). Total weight loss upon thermal decomposition to $CuInSe_2$ was 24.9%. By analogy with previously characterized hydrazinium metal chalcogenides,[14,15,23] the formula $(N_2H_4)_x(N_2H_5)_3(In_2Cu_2Se_4S_3)$ with $x \approx 0.7$ gives reasonable agreement with our results. From this formula, we expect a weight loss of 24.5% upon conversion to $CuInSe_2$, and N (11.6%) and H (2.02%), in good agreement with the empirical results.
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Figure 2. (a) X-ray diffraction pattern of bulk $CuInSe_2$ powder, prepared by decomposing the hydrazine-based precursor in a nitrogen atmosphere at 350 °C. The weak superlattice peak (211) establishes ordering of the cations on two face-centered cubic sublattices.[20] (b) X-ray diffraction pattern of a $CuInSe_2$ thin film prepared by spin casting the precursor from solution onto an oxidized silicon substrate and heating to 350 °C. The X-ray patterns were collected using Cu Kα radiation and are indexed according to JCPDS entry 40-1487. The cross-sectional TEM image of a $CuInSe_2$ thin film (c) shows lattice fringes parallel to the substrate with 3.3 Å spacing, consistent with the (112) planes.

ature, consistent with the presence of neutral hydrazine,[23] and proceeds through the loss of additional hydrazine and excess chalcogen at higher temperature, resulting in 24.9% total weight loss. The powder product (after complete thermal decomposition) is identified as the targeted $CuInSe_2$ chalcopyrite phase by powder X-ray diffraction (Figure 2a) and medium energy ion scattering (MEIS) analysis of thermally decomposed films of the precursor.

The compositional complexity and amorphous nature of the precursor make its precise description difficult. Nevertheless, the tentative overall composition, derived from the chemical and thermal analysis results, as well as from the knowledge that the final decomposition product is $CuInSe_2$, is approximately $(N_2H_4)_x(N_2H_5)_3(In_2Cu_2Se_4S_3)$ with $x \approx 0.7$,[22] implying the presence of a polychalcogenide anion. This interesting possibility is supported by the observed color change of the precursor solutions. The In_2Se_3/Se solution is

essentially colorless, and solvent evaporation yields an amorphous compound with the approximate composition $(N_2H_4)_2(N_2H_5)_2In_2Se_4$, with no evidence of a polychalcogenide anion.[15] The Cu_2S/S solution is pale yellow and, upon evaporation, yields the crystalline compound, $(N_2H_4)(N_2H_5)$-Cu_7S_4, which again gives no evidence of a polychalcogenide anion.[24] Upon mixing the Cu and In chalcogenide solutions, however, considerable darkening of the resulting solution suggests the formation of oligomerized chalcogenide anions. Polyselenide anions generally absorb in the visible to give dark green or brown solutions,[25] while polysulfides can absorb in the blue and, less strongly, in the green.[26−28] The darkening upon mixing may indicate formation of heteropolychalcogenide ions, (e.g., $S_{4−x}Se_x^{2−}$), which are also expected to absorb in the visible.[25,29] Note that, in principle, the color change could also arise from the formation of a more complex metal cation containing both Cu and In. Consequently, further studies will be required to identify the changes taking place in the mixed, precursor solution.

To prepare films, thermally oxidized silicon wafers were cleaned using a piranha process (4:1 concentrated sulfuric acid to hydrogen peroxide), and the precursor was deposited from an about 15 mg/mL hydrazine solution of the precursor by spin casting at 3500 rpm for 1 min, followed by a drying step at 100 °C for 5 min. The precursor films were converted to the semiconductor $CuInSe_2$ by heating at 350 °C for 20 min. All processing was carried out in a nitrogen-filled drybox with oxygen and water levels maintained below 1 ppm. Diffraction patterns of the $CuInSe_2$ thin films exhibit only the (112) line, indicating a strong preferential alignment of the crystalline grains along this direction (Figure 2b). Lattice fringes observed parallel to the substrate in cross-sectional transmission electron microscopy (TEM) images have a 3.3 Å average spacing (Figure 2c), consistent with the (112) planes of $CuInSe_2$.[30] Submicrometer to micrometer thick films of $CuInSe_2$, prepared on metal substrates by sputter deposition, electrochemical bath deposition, spray pyrolysis, or other techniques (all typically requiring temperatures 500 °C or higher), have shown either random orientation or the same preferred orientation seen in these thinner (10−20 nm) films prepared by spin casting with a 350 °C maximum process temperature.[30]

Controlling the stoichiometry of $CuInSe_2$ thin films is essential for optimizing its electrical properties, because the composition largely determines the concentration of donor and acceptor sites.[31,32] A slight copper deficiency is often
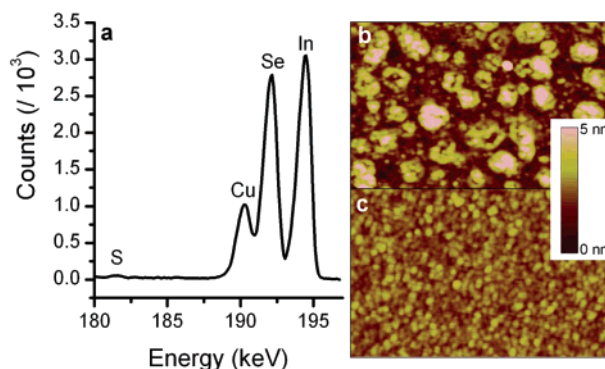

Figure 3. Composition and morphology of $CuInSe_2$ thin films. (a) MEIS analysis indicates a $Cu_{0.9}In_{1.0}Se_{1.9}S_{0.1}$ stoichiometry and 3.9 nm thickness for a film prepared as described in the text. AFM demonstrating improved homogeneity of $CuInSe_2$ films upon adding sulfur to the precursor solution: (b) 0.75 mg/mL added sulfur and (c) 1.5 mg/mL added sulfur. The film thickness is ~12 nm in each case, and the width of each AFM scan is 1 μm.

introduced to create the highest performing, single phase p-type material.[32,33] Because the precursor is prepared independently from Cu_2S and In_2Se_3, simply adjusting the mixing ratio of the two metal chalcogenides in the final solution enables control over the metal ratio in spin-cast semiconductor films. Excess chalcogen present in the precursor is lost during thermal conversion, and this decomposition process determines the overall metal-to-chalcogen ratio and the percentage of Se and S remaining in the final product.[11,22] The stoichiometry of the thin films was determined by MEIS.[34] The overall cation-to-anion ratio is 1:1 within experimental error, and sulfur is found to be preferentially lost during decomposition. Though the precursor contains a significant amount of sulfur, the product is nearly free of sulfur, having the composition $Cu_{0.9}In_{1.0}Se_{1.9}S_{0.1}$ (Figure 3a). Additional sulfur could be added to the precursor solution to tune the morphology of the thin film without significantly impacting the stoichiometry of the resulting semiconductor. The final film composition was found to be independent, within experimental errror, of the sulfur concentration used. This additional sulfur was found to improve the homogeneity and continuity of the thin films (Figure 3b) so that films from 100 nm down to 3 nm thick remained continuous.[35] The thinnest films have a grain size of ~25 nm, while films 5 nm and thicker have grains ~50 nm across, as evaluated by atomic force microscopy (AFM).

To fabricate TFTs, $CuInSe_2$ thin films were prepared on thermally oxidized silicon wafers from a precursor solution prepared as described above, with an additional 1.25 mg/mL sulfur. The heavily n-doped substrate served as a back

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(35) Thickness was determined by profilometry for thick films and AFM with verification by MEIS for thin films. Films from 50 to 100 nm thick were obtained by increasing the precursor concentration to ~115 mg/mL and varying the spinning speed between 2000 and 3500 rpm. Thicker films (up to 200 nm) were obtained by spinning a second layer of precursor on top of the first, using the same spin-casting conditions. The original film must first be thermally converted to $CuInSe_2$ to avoid redissolution. A second decomposition step was performed on the final film. The film roughness remained unchanged between layers, indicating this procedure might be extended to produce films of even greater thickness, which might be more optimal for photovoltaic applications.[19−21]
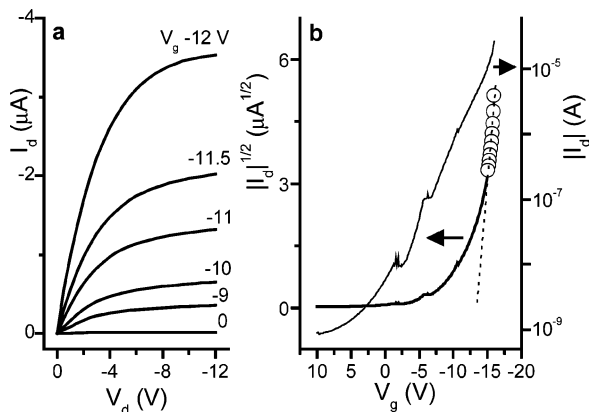
Figure 4. Current−voltage characteristics of representative CuInSe$_2$ TFT. (a) Drain current, I_d, versus drain voltage, V_d, as a function of gate voltage, V_g, for a device with channel length of 4.5 μm and channel width of 500 μm. (b) Plots of I_d and $I_d^{1/2}$ versus V_g at constant $V_d = -16$ V for the same CuInSe$_2$ transistor. The points shown were fit to the dotted line, used to calculate the saturation mobility reported in the text.

gate electrode, and gold source and drain electrodes were patterned on top of the semiconductor film by electron beam evaporation through a silicon membrane shadow mask. The resulting transistors had p-type characteristics, operating in accumulation mode upon application of a negative gate bias. Under positive gate bias, the channel is depleted of holes and the device shuts off. Post-processing transistors by immersion in a hydrazine solution[36] was found to increase conductivity without significantly affecting rectification. This process increased mobility by three to five times, while rectification remained unchanged, within the noise limitations of the measurement. A representative plot of drain current, I_d, versus drain voltage, V_d, is shown in Figure 4a as a function of applied gate voltage, V_g, for a device post-processed with hydrazine solution. The device operates at relatively low voltage (10 to 20 V) because of the thin gate oxide (40 nm); further reduction in operating voltage could in principle be achieved by using a thinner or higher dielectric constant gate insulator[37] or even a molecular gate dielectric.[38] Current−voltage curves show typical transistor behavior as I_d varies linearly with V_d initially and then saturates as the

accumulation layer is pinched off. Current modulation (I_{on}/I_{off}) and the saturation regime field-effect mobility (μ_{sat}) are calculated from the $I_d^{1/2}$ versus V_g relationship (Figure 4b)[1] to be 3×10^4 and 0.8 cm^2/(V·s), respectively.[39] The linear range mobility (μ_{lin}) can in principle be determined from the transconductance, that is, I_d versus V_g, at low V_d. However, the data fit the basic transistor model[1] poorly so we can only estimate μ_{lin} to be $\sim 5 \times 10^{-2}$ cm^2/(V·s). The difference in value between μ_{sat} and μ_{lin} arises from a field dependence of the mobility as typically found for granular organic and inorganic thin films, which may be related to hole traps at grain boundaries, at the substrate−semiconductor interface, or at the semiconductor surface.[1,11] The device characteristics depend strongly on channel thickness, which was controlled by varying the precursor concentration between 10 and 20 mg/mL. Films of 5−6 nm thickness gave optimal mobility and rectification, consistent with the diminished grain size in thinner films. In thicker films, the effective mobility is reduced and rectification hampered because the gate operates most effectively on the thin layer near the substrate.

Our results generalize high-throughput solution processing of all-inorganic TFTs to a p-type material, which is also a bimetallic chalcogenide, CuInSe$_2$. This compositional complexity allows additional tunability through control of stoichiometry. For example, we were also able to fabricate preliminary ambipolar TFTs within the same Cu$_{1-x}$InSe$_{2-y}$ material system by preparing films with a selenium deficit. Such control over doping simplifies design of complementary logic components and p−n junctions.[40]

(36) Complete transistors were immersed in 1 M hydrazine in acetonitrile for 1 h and then dried under a rough vacuum for 30 min. The resulting enhancement of conductivity may be associated with the granular nature of the films and is currently under detailed investigation.

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(39) More than a dozen substrates, each with 6−12 characterized transistors (channel length and width of ~5 to 100 μm and 0.25 to 1.5 mm, respectively) and using three different batches of precursor, demonstrated comparable mobilities and current modulation. More than 30 individual transistors on four substrates and prepared from two different batches of precursor were subjected to hydrazine post-processing and exhibited the reported enhancement of performance. Repeated cycling of individual transistors in a nitrogen atmosphere led to no noticeable degradation.

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