Low Temperature Scalable Deposition of Copper (I) Thiocyanate Films via Aerosol-Assisted Chemical Vapour Deposition

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Abstract

Copper (I) thiocyanate (CuSCN) is a stable, wide bandgap (>3.5 eV), low-cost p-type semiconductor widely used in a variety of optoelectronic applications, including thin film transistors, organic light-emitting diodes and photovoltaic cells. For CuSCN to have impact in the commercial fabrication of such devices, large area, low-cost deposition techniques are required. Here, we report a novel technique for deposition of CuSCN that addresses these challenges. Aerosol-assisted chemical vapour deposition (AACVD) is used to deposit highly crystalline CuSCN films at low temperature. AACVD is a commercially viable technique due to its low cost and inherent scalability. In this study the deposition temperature, CuSCN concentration and carrier gas flow rate were studied and optimised, resulting in homogeneous films grown over areas approaching 30 cm². At the optimised values *i.e.* 60 °C using a 35 mg/ml solution and a carrier gas flow rate of 0.5 dm³/min, the film growth rate is around 100 nm/min. We present a thorough analysis of the film growth parameters and the subsequent morphology, composition, structural and optical properties of the deposited thin films.

Introduction

Copper (I) thiocyanate (CuSCN) is a p-type semiconductor suitable for large scale deposition owing to its ease of processing, chemical stability and exceptionally low cost ¹. Additionally, the high intrinsic hole mobility ($\sim 0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), crystallinity and large bandgap ($> 3.5 \text{ eV}$) have made it attractive in device applications ^{2,3}. The p-type nature arises from a stoichiometric excess of thiocyanate ions, which induce copper ion vacancies within the crystal structure and also leads to widening of the bandgap ^{1,4}.

Determining the optimum processing conditions is vital to obtain the desired optical and electrical properties of CuSCN. However, the limited solubility of CuSCN makes it difficult to achieve this. N-propyl sulfide solvents were introduced by Kumara *et al* for deposition of CuSCN which was subsequently followed by numerous reports using dipropyl sulfide (DPS) ^{5–7}. The high boiling point (b.p.) of DPS ($> 140 \text{ }^\circ\text{C}$) requires high annealing temperatures to evaporate the solvent and crystallise the film, rendering it undesirable for many temperature sensitive materials. Furthermore, the low solubility in DPS means that thin, inhomogeneous films are often formed ². Other solvents have generated films of improved quality, particularly diethyl sulfide (DES), which has a higher solubility limit ($\sim 40\text{--}50 \text{ mg/ml}$) and lower b.p. ($92 \text{ }^\circ\text{C}$) than DPS ^{8–10}.

Numerous deposition techniques have subsequently been reported for the preparation of CuSCN thin films, these include spin coating, spray coating, drop casting, doctor blading, ink-jet printing and electrochemical deposition ^{7,11–15}. Device applications mandate that CuSCN thin films should be smooth and continuous, free from macroscopic defects and microscopic pinholes. However, many of the deposition methods reported yield discontinuous films that are difficult to reproduce, thus spin coating is still the preferred technique for film growth ². Although spin coating results in favourable film properties, it is unsuitable for large-scale deposition of CuSCN, making the need to find an alternative essential. Thus, the research conducted in this study investigates whether aerosol-assisted chemical vapour deposition (AACVD) could be a suitable alternative deposition technique.

AACVD is a variant of conventional chemical vapour deposition techniques, eliminating the need for high vacuum during growth by introducing liquid aerosols in an inert gas medium to deposit a film ¹⁶. The ambient-pressure technique utilises control of the inert gas flow rate,

precursor concentration and deposition temperature for facile control of film growth. Aerosol droplets, created using an ultrasonic mister, are carried in a N₂ gas flow into the reactor and are predominantly deposited onto the heated substrate rather than the cold walls of the reactor. AACVD is inherently reproducible and allows large-scale deposition of a variety of materials with high growth rates. Furthermore, limitations of CuSCN solubility and solution processability are overcome using AACVD as the technique affords the use of high boiling point solvents, as the necessary aerosol formation depends solely on the surface tension of the solvent. AACVD has previously been used to deposit a variety of semiconductor thin films, including MoS₂, SnS, CdSe, Cu₂ZnSnS₄ (CZTS) and more recently CuO_x^{17–22}. Here, we report for the first time the deposition of CuSCN using AACVD.

Here we report the influence of varying the major processing variables (deposition temperature, CuSCN concentration and carrier gas flow rate) on thin film formation. This is accompanied by a complete analysis of the film growth process and the subsequent morphology, composition, structural and optical properties of the deposited thin films.

Experimental Section

Fluorine doped tin oxide (FTO) coated glass (NSG TEC 15) from Pilkington was washed consecutively with a clear surfactant, acetone and isopropanol then dried under a N₂ stream before UV-Ozone cleaning. Copper (I) thiocyanate (CuSCN, 99 %) and diethyl sulfide (DES, 98 %) were purchased from Sigma Aldrich and used as received. AACVD of CuSCN involved a single-step deposition using solutions of 25, 35 and 45 mg/ml that had been prepared in advance and stirred overnight before finally being filtered through 0.45 µm PTFE filters. Depositions were conducted using a custom-made stainless steel reactor (**Figure S1**) at different temperatures ranging from 40 - 100 °C under a N₂ flow rate of 0.25 - 1 dm³/min. The temperature was controlled via a Eurotherm 3216, using two type-K thermocouples inserted into a graphite block onto which the substrates were directly placed. A uniform deposition area of 28 cm² was identified and substrates were placed in this area during the study.

Scanning electron microscopy (SEM) was used to study the surface and cross-sectional morphology of the deposited films. Images were acquired via an in-lens electron detector using a LEO Gemini 1525 field emission SEM operated at 5 kV. Prior to imaging, films were sputtered with 10 nm of Cr to minimise charging and improve image quality. Energy-

dispersive X-ray spectroscopy (EDX) was used for elemental mapping of the samples. The spectrum was generated using a 20 kV electron beam and sampled using an INCAx-act SDD detector (Oxford Instruments). Surface roughness and film thickness (by etching) was analysed using a Veeco DEKTAK 150 profilometer with a scan resolution of 0.042 $\mu\text{m}/\text{sample}$. Surface roughness and topography was further analysed using an Agilent 5500 atomic force microscopy (AFM) in tapping mode. The topography scans were achieved using a scan speed of 0.5 lines/sec and a resolution of 512 points/line. The data was analysed using Gwyddion software.

Optical property studies were performed by analysing the absorption spectra over the range 250-1000 nm. The absorption spectra were acquired using a Perkin Elmer Lambda 25 UV-Vis spectrometer (UV-Vis).

Structural properties were determined using X-ray diffraction (XRD) diffractograms of the films. The data was obtained using a PANalytical X'Pert-Pro diffractometer using Ni-filtered Cu $\text{K}\alpha_1$ and Cu $\text{K}\alpha_2$ X-rays. Diffractograms were obtained from 5 - 50° 2 θ with a step size of 0.016°.

Results and Discussion

Temperature was first investigated over the range 40 – 100 °C. For this initial study the CuSCN concentration and N₂ carrier gas flow rate were fixed at 35 mg/ml and 0.5 dm³/min respectively. **Figures 1a-e** show SEM micrographs of the typical film morphologies deposited over this temperature range. Our initial hypothesis was that at temperatures around 100 °C film formation would be most likely as this is slightly higher than the b.p. of DES: using AACVD evaporation of the solvent whilst preventing rapid aggregation of material is essential to form a uniform crystalline film ²³. However, **Figures 1a-b** show the nucleation and growth of spherical agglomerates that increase in size as temperature decreases. This is known to occur at excessively high deposition temperatures, where, due to the high surface area to volume ratio of the aerosol droplets, the solvent evaporates rapidly leading to homogeneous nucleation (in the gas phase) and production of spherical agglomerates ²³. In parallel we also observed that significant deposition on the reactor walls was occurring at 80 – 100 °C, a clear indication that these temperatures are excessive. Reducing the temperature to 60 °C results in complete substrate coverage, **Figure 1c**. Further reducing the temperature to 40 °C results

in films being formed with different morphologies observed on the same substrate, **Figures 1d-e**. **Figure 1d** shows a droplet shaped structure from aerosol droplets being directly deposited onto the substrate whilst **Figure 1e** represents long plate-like structures from CuSCN precipitating from larger volumes of solution that have built up on the substrate. Both these effects result from the temperature being too low to evaporate the solvent prior to deposition, resulting in droplets of precursor solution being deposited onto the substrate, rather than a chemical vapour. Thus, from this study 60 °C was identified as the optimum temperature. **Figure 1f** shows an EDX spectrum for the 60 °C film confirming the presence of Cu, S, O and Sn, the latter originating from the FTO substrate.

Figure 1. SEM micrographs (a-e) of films prepared at the temperatures indicated, showing the significant variation in the morphology and surface coverage (scale bar 5 μ m). EDX analysis (f) shows the elemental composition of a 60 °C film.

Elemental maps for films grown at 40 and 60 °C are shown in **Figure 2**, the 60 °C films clearly shows a uniform elemental distribution consistent with the uniform film morphology observed by SEM. In contrast, the film prepared at 40 °C shows localisation of Cu and S in the aggregate with large regions of uncoated FTO between aggregates. The aggregates are indicative of CuSCN precipitating from solution over time. Therefore, we conclude that 60 °C is the optimum deposition temperature to produce a uniform film, and that the temperature window for film formation is within $\pm 20^\circ\text{C}$.

Figure 2. Elemental mapping of 60 °C (top) and 40 °C (bottom) film via EDX. Images highlight the presence of main elements copper (Cu), sulphur (S), oxygen (O) and tin (Sn) (scale bar 40 μ m).

X-ray diffraction (XRD) patterns of a CuSCN film deposited at 60 °C and a reference CuSCN powder are shown in **Figure 3a**. There is a strong contribution to the film XRD pattern from the FTO substrate owing to the low film thickness. This is not observed with the powder reference as it is measured on single crystal Si holder that is cut off-axis. The major peaks (003), (101), (006) and (110) seen in the AACVD CuSCN film match well with the reference pattern and correspond to β -CuSCN, which is the desired phase for optoelectronic applications¹⁰.

A range of band gap values ($\sim$ 3.6-3.9 eV) have been reported for CuSCN due to subtle differences in deposition technique, film surface morphology and method used to measure the band gap^{5,24–26}. **Figure 3b** shows the optical absorption spectra for a CuSCN film deposited at 60 °C. The spectrum shows an absorption edge around 320 nm, which agrees well with literature²⁷. In **Figure 3c** Tauc plots are used to calculate the bandgap of the film. These are calculated as 3.73 eV and 3.62 eV for direct and indirect bandgap values respectively²⁸. We report both values as there is debate in current literature as to whether the lowest transition in CuSCN is direct or indirect⁵. Thus, the structural and optical properties of the AACVD prepared films agree well with existing literature reports of films prepared by other methods.

Figure 3. XRD plots (a) of AACVD CuSCN and β -CuSCN reference powder. UV-Vis absorbance data (b) and corresponding tauc plot (c) for AACVD CuSCN allowed calculating the direct and indirect band gap to be ~ 3.73 eV and ~ 3.62 eV, respectively.

Next we consider the influence of carrier gas flow rate over the range $0.25 - 1 \text{ dm}^3/\text{min}$ whilst holding the deposition temperature at the optimised value of 60°C and the CuSCN concentration at 35 mg/ml . The goal was to produce a thinner and smoother film, as this is desired for optoelectronic applications.

Representative SEM images of the films prepared are shown in **Figure 4**, where significant differences in the surface morphology and thickness are observed. At the lowest flow rate ($0.25 \text{ dm}^3/\text{min}$) incomplete film formation is observed with large, partially-interconnected domains with large areas of exposed FTO visible. It is known with AACVD that precursors diffuse through a boundary layer before being adsorbed onto the surface of the substrate

^{29,30}. Illustrated in **Figure S1**, the boundary layer exists due to the difference in flow velocity between substrate surface and the bulk of the flow ³¹. In this case, as the deposition temperature and precursor concentration are kept constant, the boundary layer is solely influenced by the flow rate. At lower flow rates, the film characteristics are indicative of turbulent flow occurring within the reactor, leading to a smaller boundary layer, thus allowing droplets of the solution to wet the substrate heavily promoting the formation of small islands of CuSCN.

At the highest flow rate (1 dm³/min) larger regions of CuSCN are formed creating an inhomogeneous film with significant areas of FTO exposed. This is indicative of a large boundary layer, where during growth there is less time for the depositing material to diffuse through the boundary layer to the substrate. Instead, significant quantities of the CuSCN are flushed through the reactor to the exhaust. The island like growth observed at 0.25 and 1 dm³/min result in a large surface roughness, > 1 μm, in both sets of films.

A flow rate of 0.5 dm³/min results in a balance being achieved between the depth of the boundary layer and amount of time it takes for deposition. At 0.5 dm³/min laminar flow results, which produces uniform films with no areas of exposed FTO. The average film thicknesses, taken from surface profilometer and SEM measurements are around 1.5 μm with an average root mean squared (RMS) roughness of 92 nm as determined by AFM, **Figure S2**.

Figure 4. SEM topographic morphology (top) and cross-section (bottom) micrographs showing coverage at different nitrogen flow rates (scale bar 2 μm). This showed an optimum flow rate of 0.5 L/min formed a uniform film.

The final growth parameter to be investigated was the CuSCN concentration, using 25, 35 and 45 mg/ml whilst maintaining temperature and carrier gas flow rate at 60 °C and 0.5 dm³/min respectively. Here the film thickness was plotted against growth time to establish the film growth rate as concentration is varied, **Figure 5a**. This is now possible as the other, optimised, growth parameters allow the formation of relatively flat and continuous films. The SEM images obtained following 15, 25 and 35 minutes of growth show how the film morphologies are changing with time, **Figure 5b**. As anticipated the volume of material increases with increased deposition time and island growth (Vollmer-Weber) is occurring, a typical growth mechanism for AACVD films ³². The XRD patterns, **Figure S3**, show an increase in the volume of crystalline material with increased growth time.

At 25 mg/ml, the reduced concentration of CuSCN in the aerosol means a reduced film growth rate. The solvent rich aerosol may also cause recrystallisation as the film thickness grows. Complete coverage was achieved after 35 minutes, with the calculated growth rate after complete film formation found to be 29 ± 7 nm/min. A concentration of 45 mg/ml resulted in complete film coverage after 30 minutes of growth. This is, however, offset by the formation of larger islands that result in very rough films. Here CuSCN is approaching its solubility limit, hence the highly concentrated solution leads to the nucleation and growth of larger islands. Under these conditions a film growth rate after complete film formation was found to be 93 ± 9 nm/min. At 35 mg/ml complete film formation occurs following 25 minutes of deposition with a significant reduction in roughness as film growth continues. These growth conditions favour a balance between solution saturation and film nucleation, resulting in a high growth rate of 102 ± 4 nm/min. Thus, it is concluded that 35 mg/ml is the optimal concentration for uniform film formation.

Figure 5. Plots of measured film thickness versus time (a), the dashed vertical line indicates the time taken for complete film coverage of the substrate, SEM micrographs (b) showing the influence of solution concentration and growth time on film microstructure (scale bar 4 μm).

Having identified the optimum growth parameters, film uniformity across the entire reactor area was investigated. A surface profilometer was used to measure film thickness at 30 points across the film surface. The contour plot, **Figure 6**, maps the thickness variation across the 40 cm^2 area of the substrate. This is only limited by the surface area of our heating block which is more than adequate for lab-scale deposition but could be easily increased in size. Here subtle variations in thickness are observed, particularly near the reactor inlet where there is insufficient substrate-aerosol interaction time to allow for film growth, and again towards the end of the reactor where material accumulation appears to be occurring. On the whole deposition is rather uniform across 28 cm^2 of the large reactor area, which is highly encouraging when considering scale-up of this process.

Figure 6. Contour plot of the CuSCN film thickness across the length of the reactor. Precursor aerosols flow into the reactor from the left (inlet).

Conclusion

This study demonstrates that CuSCN films can be successfully deposited using AACVD. Through exploration of the critical growth parameters we have identified a series of optimum growth parameters that result in the formation of large area, continuous films of low roughness. The critical growth temperature, concentration and carrier gas flow rate are 60 °C, 35 mg/ml and 0.5 dm³/min respectively. Under these conditions highly reproducible films are formed, demonstrated with growth over a 28 cm² area. Detailed analysis of film growth reveals that growth proceeds by Volmer-Weber type growth which appears to dominate under all of the reaction conditions investigated. Given the uptake of CuSCN as a novel p-type semiconductor and the demonstration of its excellent optoelectronic properties in a range of device platforms we anticipate that the demonstration of such large area deposition will further enhance the appeal of this material.

Supporting Information

AACVD reactor schematic, reactor specifications and additional characterisation data (AFM film topography and XRD of film evolution) are supplied as Supporting Information.

Dedication

We dedicate this paper to Dr Russell Binions, who was the academic supervisor for Lokeshwari. She was just beginning her scientific journey as his life came to an end. An incredible co-author, colleague, supervisor and friend who is dearly missed.

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