



Improved CuSCN–ZnO diode performance with spray deposited CuSCN

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ABSTRACT

P-type copper(I) thiocyanate (β -CuSCN) was deposited using a pneumatic micro-spray gun from a saturated solution in propyl sulphide. An as-produced $6\ \mu\text{m}$ CuSCN film exhibited a hole mobility of $70\ \text{cm}^2/\text{V}\cdot\text{s}$ and conductivity of $0.02\ \text{S}\cdot\text{m}^{-1}$. A zinc oxide (ZnO) nanorod array was filled with CuSCN, demonstrating the capability of the process for filling nanostructured materials. This produced a diode with a n-type ZnO and p-type CuSCN junction. The best performing diodes exhibited rectifications of $3550\ \text{at}\ \pm 3\ \text{V}$. The electronic characteristics exhibited by the diode were attributed to a compact grain structure of the β -CuSCN giving increased carrier mobility and an absence of cracks preventing electrical shorts between electrode contacts that are typically associated with β -CuSCN films.

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1. Introduction

Hexagonal copper(I) thiocyanate (β -CuSCN) has been reported as an inorganic p-type semiconductor with a wide band-gap of $3.6\ \text{eV}$ [1]. This material exhibits good optical transparency to the visible spectrum, chemical stability and has a previously reported hole conductivity of $1.4\ \text{S}\cdot\text{m}^{-1}$ with hole mobility of $1.08\ \text{cm}^2/\text{V}\cdot\text{s}$, after doping [2]. These properties have led to the incorporation of CuSCN into various optoelectronic devices including dye-sensitized solar cells [2–4] and nanostructured photovoltaic devices [5–7], as well as studies to improve the p-type conductivity and hole concentration [1,8,9].

Zinc oxide (ZnO) nanostructures provide a wide band-gap material that has a high surface area and has been shown to be suitable for various applications such as optoelectronics [2], piezoelectric devices [10], gas sensors [11] and field effect transistors [12]. Numerous techniques have been applied to CuSCN deposition in order to achieve good pore-filling of nanostructured materials such as ZnO or TiO_2 . Electrochemical deposition was reported to fill between the ZnO nanorods, however rectifications of $154\ \text{at}\ \pm 2\ \text{V}$ [13] and $19\ \text{at}\ \pm 0.5\ \text{V}$ [14] indicate a poor diode performance. Successive ionic layer adsorption and reaction of CuSCN was reported to result in poor pore-filling of nanostructured surfaces [3]. Chemical bath deposition was used to

deposit CuSCN films [15] but pore-filling of nanostructured surfaces was not reported.

To date, the most common method for CuSCN deposition is that of impregnation [4,16–18]. This involves dissolving CuSCN in n-propyl sulphide (n-PS) and drop-coating the solution onto a heated (65 – $80\ ^\circ\text{C}$) surface. Solution concentrations varied from $0.05\ \text{M}$ [19] to an excess of CuSCN [4]. The process typically results in uneven deposition over the surface due to the uncontrollable rate of deposition. Mud-cracking of the CuSCN film is often observed, which leads to electrical shorts and poor device performance [20]. The mud-cracking is linked to the slow evaporation of n-PS from the CuSCN film, forming cavities and voids.

Here we present a direct comparison of diode performance between the impregnation technique and a micro-spray technique. A significant enhancement in device performance is seen for the spray-coated diodes. This is related to the morphological and crystallographic properties, which differ between the two deposition techniques.

2. Experimental details

All the (Sigma-Aldrich) reagents were analytical grade and used as received. Fluorine-doped tin oxide (FTO) coated glass substrates were cleaned thoroughly with acetone and isopropanol using an ultrasonic bath. A $0.005\ \text{M}$ zinc acetate in ethanol solution was used to deposit a ZnO seed layer onto FTO substrates. This was then annealed at $350\ ^\circ\text{C}$ for 25 min. The process was repeated three times [21]. A pH 10.8 aqueous solution consisting of $0.2\ \text{M}$ ammonium hydroxide, $0.02\ \text{M}$ zinc nitrate and $0.07\ \text{M}$ hexamethylenetetramine was mixed in a

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sealable glass vessel. The seeded substrates were suspended using a polytetrafluoroethylene stand in the aqueous solution, seed-layer facing down. The sealed vessel was placed in an oven (Town & Mercer) for 4 h at $90\text{ }^{\circ}\text{C} \pm 3\text{ }^{\circ}\text{C}$. The process was repeated eight times with fresh solutions to obtain the desired aspect ratio of 1:30. The substrates were rinsed using deionised water and dried with N_2 before annealing at $400\text{ }^{\circ}\text{C}$ for 1 h in air.

A saturated solution of CuSCN was produced by dissolving 0.200 g in 10 ml n-propyl sulphide. This was stirred for 24 h at room temperature and allowed to settle for 12 h. Samples were placed on a hotplate, which was angled at approximately 45° and set to $85\text{--}90\text{ }^{\circ}\text{C}$ throughout the deposition. Spray deposition was performed using a pneumatic spray gun (IWATA Custom Micron) with a $20\text{ }\mu\text{m}$ -sized nozzle that directed a micro-fine mist onto the heated substrate (Fig. 1-A). Using a sweeping side-to-side motion the CuSCN spray was deposited at a pressure of 0.1 MPa for 10–20 seconds. The nozzle setting on the spray gun was set to 2 on the first turn. The n-propyl sulphide solvent can be harmful if inhaled and so for safety measures the experiment was conducted in a fume hood. We term the process spray deposition. Impregnation deposition was performed as reported in ref. [6] using the same saturated solution. To complete the device a 0.1 cm^2 gold electrode was sputtered onto the top surface (Fig. 1-B).

Characterisation was performed using an FEI Inspect-F scanning electron microscope (SEM) to analyse the surface and interface morphology at an operating voltage of 20 kV. Glancing incidence X-ray diffraction (GIXRD) was performed with a Siemens D500 using $\text{CuK}\alpha$ radiation ($\lambda = 0.1540\text{ nm}$) under a glancing angle configuration of 3° with 2-D sample rotation.

Hall effect measurements were conducted via the Van der Pauw method. CuSCN was spray-coated onto clean 1 cm^2 square glass substrates. Gold was sputtered to form right-angle triangles in each corner before mounting using silver paint onto a printed circuit board for testing. Hall mobility was taken from an average of 10 measurements with the compliance voltage set to 5 V, a measuring current of $0.03\text{ }\mu\text{A}$ and magnetic field of 0.5 T.

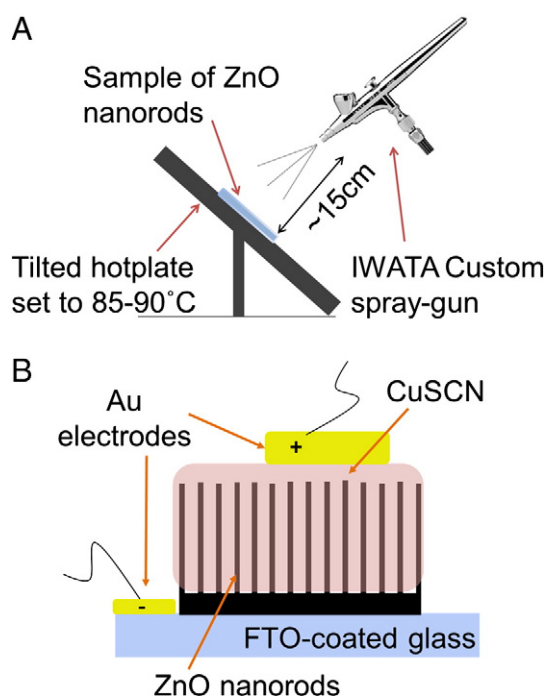


Fig. 1. Schematics showing A) the experimental arrangement for CuSCN spray-deposition and B) the completed ZnO nanorod-CuSCN diode.

Current-density vs. voltage (J-V) characteristics of the devices were obtained in the dark using a Keithley 2400 and controlled using Labview 8.2 software.

3. Results and discussion

Spray-coating produced a high density of evenly distributed 40 nm CuSCN grains on the nanorod surface (Fig. 2-B1), while impregnation generated sporadic coverage of 120 nm grains (Fig. 2-A1). It would be expected that larger grains of CuSCN would offer a lower series resistance due to the lower number of grain boundaries. However, as evaporation of n-PS is slow [5] the evaporation process leads to voids and gaps between the grains of CuSCN which increases the resistance of the layer. While using the $20\text{ }\mu\text{m}$ spray-gun a fine-mist of the saturated CuSCN solution is generated, this allows evaporation of n-PS to occur prior to contacting the ZnO surface. The small droplets of CuSCN solution that are formed become supersaturated and will nucleate on contact with the heated surface, where there will be a rapid evaporation of the n-PS. This minimises the amount of n-PS trapped in the grains leading to a compact and uniform coverage of CuSCN over the ZnO nanorods (Fig. 2-B2). Unlike previous CuSCN devices deposited using the impregnation technique, device performance did not change over the time that the devices were tested: a device tested within minutes of CuSCN coating performed in an identical manner to a nine-month old device. This demonstrates that little n-PS is trapped in the CuSCN using the spray technique. Deposition is complete when a smooth and even top-surface is observed by eye. In this case it required 150 spray steps; however this is dependent on the nanostructure. SEM analysis shows no observable mud-cracks (Fig. 3 inset). In addition to the improved morphology, by removing the drying steps during processing and the storage time typically required to generate acceptable device performance [22,23], we have significantly simplified and increased the speed of the process. For comparison, bare nanorod surfaces and cavities between CuSCN grains were observed for the impregnation-deposition method (Fig. 2-A2). The irregular grain-sizes and coverage led to a rough, uneven top-surface. Spray-deposition produced good pore-filling of the ZnO nanorods, maximising contact at the ZnO-CuSCN interface (Fig. 3). However, the high density and irregular alignment of the nanorod array prevented the CuSCN mist from penetrating to the very base of the nanorods.

GIXRD analysis of the ZnO-nanorod/CuSCN heterostructure confirms the peaks match those of β -phase CuSCN (JCPDS 29-581) and hexagonal wurtzite ZnO (JCPDS 79-0207) (Fig. 4). The full-width half-maximum of the CuSCN XRD peaks is larger for spray-deposition (Table 1) which is consistent with the smaller grain size.

To determine the electrical characteristics of CuSCN deposited via spray coating a glass substrate was coated with CuSCN in a range of film thicknesses ($100\text{--}700\text{ nm}$). Control over the deposition rate is reflected by the decreasing optical band-gap ($3.79\text{--}3.87\text{ eV}$), gradually approaching that of bulk CuSCN as the layer increases in thickness (Fig. 5). Thin film interference fringes were observed to occur prior to the absorption onset (inset Fig. 5) which confirms uniformity and evenness of layers deposited onto the substrate.

A semi-log J-V plot of the ZnO/CuSCN diodes tested the same day as fabrication shows rectifications of 1240 and 3550 at $\pm 3\text{ V}$ for impregnation and spray-deposition, respectively (Fig. 6). This enhanced diode performance has been attributed to improved pore-filling and improved contact with the nanorod structure. The performance is further enhanced due to improved carrier mobility as shown by Hall analysis (see below). Our best rectifications are approximately ten times better than those previously reported for ZnO-CuSCN diodes [13], and the same order of magnitude as recent NiO-ZnO p-n-heterojunctions at an applied bias of 1 V [24].

Hall effect measurements were performed to assess the conductivity of spray-deposited CuSCN films. CuSCN film-thickness was determined using SEM cross section analysis. For a $6\text{ }\mu\text{m}$ film, Hall

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