Chapter 6
CZTS nanocrystalline ink: synthesis and device fabrication

6.1 Introduction

6.1.1 Nanocrystalline inks as PV absorbers

The previous chapter outlined the synthesis and characterization of chemical bath deposited (CBD) CZTS nanostructured films. However, there are certain problems with procedures like CBD, sol-gel synthesis, SILAR and electrodeposition such as disparity in film parameters when synthesized in a large number of batches, differences in thickness of the CZTS layer from batch to batch and variation in stoichiometric composition between batches. Also, films synthesized by the above methods have shown a tendency to start peeling off the substrate after being stored for a few months which is damaging to the device. The current chapter therefore details the synthesis, optimization, device fabrication and device testing of solar cell devices using solution-processed nanocrystalline (NC) inks. These inks are easily prepared at a low cost, the synthesized volume can be scaled up while maintaining the correct stoichiometry, their homogenous deposition on any substrate can be carried out using a simple hand-held spraying device, and inks as well as films synthesized as a part of this study have remained stable even after almost one year of their synthesis. The biggest advantage of these inks is their ability to be readily incorporated into a roll-to-roll type printing process for the fabrication of large-scale flexible, low-cost solar cells. CZTS based NC inks are therefore one of the most promising options for a material system that has mild processing conditions, uses inorganic materials and so promises high device efficiencies, are photostable over long periods of time and can be seamlessly integrated into a high-throughput device fabrication process.

Molecular precursors are used for the synthesis of nanocrystalline inks using the process of “arrested precipitation” in a solvent kept at a high temperature that acts a coordinating agent. These
NCs are fundamentally of a core-shell type structure with a core composed of the inorganic nanocrystal of the desired material and a shell of an organic ligand that is chemisorbed onto the core to which allow these inorganic crystals to form a stable dispersion in organic solvents and prevents their aggregation. These inks are then deposited on a substrate using one of many techniques such as spraying, spin-coating, doctor-blading etc. and then either heated or the solvent is allowed to evaporate leaving behind a dry NC layer or film.

A large number of ternary and quaternary compounds have been reported in the form of NC inks such as CuISe<sub>2</sub> (Panthani et al., 2008; Guo et al., 2008), CuIS<sub>2</sub> (Panthani et al., 2008; Li et al., 2010), CuAsS<sub>4</sub> (Balow et al., 2015), CuGaSe<sub>2</sub> ((Panthani et al., 2008), Cu<sub>2</sub>SnS<sub>3</sub> (Vanalakar et al., 2015; Tang et al., 2008), and more recently, CIGS (Panthani et al., 2008; Guo et al., 2013; McLeod et al., 2015) and CZTS (Zhou et al., 2013; van Embden et al., 2014; Miskin et al., 2014). Out of all of these, it is CIGS in particular which has exhibited the highest efficiencies till date with 15% efficient CIGSSe NC ink based cells being reported (McLeod et al., 2015). However, the fact that CIGS is composed of two rare and expensive elements, (indium and gallium) don’t allow it to be a viable choice for large scale solar cell applications. Therefore a lot of research is instead focusing on CZTS NC ink synthesis and device optimization with particular interest in defect removal and doping to enhance device performances.

6.1.2 CZTS based nanocrystalline inks

CZTS NCs have been synthesized using oleylamine (OLA) as a solvent and capping agent and the effect of the reaction temperature was studied. It was shown that at a temperature below and equal to 260°C, the kesterite phase was formed while at ~275°C and above wurtzite was formed. It was also shown that NCs which were zinc-rich and sulphur poor had a lesser amount of ZnS present in it and had a change in resistivity of ~10<sup>4</sup> k/cm when it was illuminated (Zhou et al., 2013). Another study examined the effect of solvent on the phase and shape of CZTS NCs and found that two parallel phases existed for CZTS of wurtzite and kesterite when DDT (1-dodecanethiol) was used as a solvent however as a larger amount of OLA was added the kesterite phase decreased along with the NCs becoming smaller and uniform in shape. As the amount of OLA added was increased
it was seen that the NCs became more wurtzite and their shape changed to finally become ‘rice grain like’ with a pure wurtzite phase. This kind of a growth was explained on the basis of an “asynchronous doping and formation” mechanism. It was also shown (through Hall measurements) that the rice-grain like NCs had better electronic transmission and therefore it was proposed they may give a higher photocurrent and therefore a more efficient device (Li et al., 2012). The effect of synthesis time has also been examined and it has been shown that there are primarily two types of particle populations that exist as soon as synthesis begins and these are large particles of copper and zinc and smaller ones of copper and tin. From this starting population, growth time plays the deciding role as to what is the final size and quality of the NCs formed. It was shown that the longer the synthesis time, the higher the NC yield and more stoichiometrically accurate the chemical composition (Collord et al., 2015). The use of other solvents for CZTS NC ink synthesis has also been reported such as DMSO (dimethyl sulfoxide) which reduces the carbon content in the material (which as explained earlier causes a fall in device performance) and is non-toxic unlike hydrazine which is also used for the same purpose but is extremely dangerous (Wang et al., 2015); also, a mixture of water and ethanol has been used to synthesize a CZTS colloid which was sprayed on a substrate followed by nitrogen annealing and then selenization to give a final device efficiency of 8.6% (Larramona et al., 2014). However, it is CZTSSe which gives the best device efficiencies and most current research focuses on utilizing and optimizing devices based on this.

Recently, a study has reported 9% efficient CZTSSe devices based on selenization of film made of CZTS NCs. The improvement in device performance has been attributed to nanoparticles that are compositionally more uniform and an optimized selenization procedure leading to micron-scale, large grains for the absorber layer and minimized thickness of the fine grain layer that develops between the larger grain layer and molybdenum (and leads to fall in device efficiency). These improvements have been said to lead to a higher short circuit current and fill factor (Miskin et al., 2014). The effect of particle size distribution in the ink has been demonstrated and in this study two populations of particles were identified each of which were showed size-dependent variation in composition. Particles from each of the populations as well as a mixture of the particles were
independently selenized and formed into devices and it was seen that the final films showed a large amount of ‘phase-segregation’ in the case of particles from individual populations whereas the film made by mixed particles was more homogenous. In terms of device efficiencies it was seen that particles of the individual populations gave varying performances but devices made using the mixed particles showed up-to 7.9% efficiency. When the precursor recipe was optimized to yield particles with narrower compositional variation, the efficiency improved further to 8.4% (Carter et al., 2014).

Another study has reported 7.7% efficient CZTSSe devices based on a technique which does not involve the use of coordinating solvents such as pyridine or hydrazine and is based on a process of ligand exchange which allows the dispersion of CZTS in environmentally safe, non-toxic solvents such as ethanol and propanol (van Embden et al., 2014).

It has also been shown that cracking of CZTSSe films which happens due to ligand exchange after each spin coating can be avoided by adopting a combination of techniques that involves processes using ligand exchange and no ligand exchange. Also it was shown that a homogeneity of the film could be improved by having a two-stage annealing process. It was also shown that this modified processing gave films which had a large grain layer at the top and a finer nanoparticle layer at the bottom and this was due to diffusion of copper and zinc from the bottom to the surface and accumulation of carbon near the bottom (Lin et al., 2015). Band gap tuning in CZTS has been demonstrated by the gradual replacement of the $S^2$ ion by $Se^2$ to give CZTSSe. It is also shown through Raman spectroscopy that the sulphur plays a very important role in governing the vibrational modes of the material and that as sulphur content is decreased from 0.76 to 0, the band gap decreases from 1.3 eV to 0.9 eV (Li et al., 2015). Photoluminescence and surface photovoltage spectroscopy measurements made on CZTSSe films with varying ratios of $S/(S+Se)$ were carried out and showed the presence of possible intrinsic point defects which were indicated by the observation of activation energies below 150 meV (in the photoluminescence) and 90 meV and 300 meV (in the surface photovoltage spectroscopy) (Lin et al., 2015).
6.1.3 Additional treatments for CZTS NC films

Apart from optimizing absorber layer synthesis, another very important aspect in the application of CZTS NC inks is the use of surface treatments to enhance the existing device performance. Potassium cyanide (KCN) has been successfully used as an etchant to improve the surface band gap of CZTS from ~1.5 eV ~1.9 eV by preferentially etching copper and to a lesser extent tin (Bär et al., 2011); similarly another study used Kelvin probe force microscopy with Raman spectroscopy to show that out of secondary phases like Cu$_x$S, ZnS and MoS$_2$ present on the films surface, KCN treatment removed the Cu$_x$S phase and the resulting device gave an efficiency of ~5% which was attributed to efficient charge separation and a higher work function leading to a better Voc (Kim et al., 2015). In the way, KCN has been shown to remove the unwanted Cu$_x$S phase, a hydrochloric acid (HCl) treatment has been demonstrated to remove the ZnS phase in zinc-rich CZTS. This study showed that zinc-rich CZTS which is desirable for a better device performance but suffers from an excess of ZnS formation which doesn’t allow the efficiency to be as high as it can, may be treated with a HCl based solution which selectively removes ZnS. Devices which had been given this treatment showed an efficiency of ~5.2% which was almost two times that of devices without the HCl treatment (Fairbrother et al., 2012). However, the most commonly used treatment is based on incorporation of sodium into the CZTS layer, this can be through a surface treatment using a sodium chloride (NaCl) solution or through by annealing a soda-lime glass substrate which allows the sodium to diffuse up into the CZTS film or by adding sodium salts during synthesis. The beneficial effect of sodium addition to CIGS solar cells has already been demonstrated and studies have proven using x-ray diffraction, Hall measurements and x-ray photoelectron spectroscopy that that doping CIGS absorber layers with sodium dramatically increased the hole concentration over a wide range of Cu/(In+Ga) ratios (Nakada et al., 1997; Kronik et al., 1998). Similarly, in the case of CZTS, inclusion of sodium has been shown to be beneficial in many ways. The presence of sodium has shown to greatly enhance the grain growth of CZTS as well as to significantly affect its electronic properties. It has been suggested that electronically “active” defect states can be either introduced or removed from CZTS if sodium is present at the grain boundaries. This can be possible
by making the acceptors shallower (or reducing recombination) which takes place when donors and deep defects get passivated by the sodium. This in turn would lead to an increase in Voc and the fill factor (Sutter-Fella et al., 2014). However, large grains will have fewer grain boundaries and consequently on cooling, the sodium will diffuse out and segregate on the surface. It has also been shown that there is a higher surface potential at the grain boundaries of CZTSSe films as compared to on the grain itself and conducting AFM has shown that there is increased current flow near these boundaries, this in the case of a p-type material means that there is an increased minority-carrier collection near the boundaries (Li et al., 2012) with the same effect having previously been seen in CIGS films (Jiang et al., 2004). This would mean therefore that holes are being repelled, therefore aggregation of sodium at grain boundaries will increase the carrier collection. In another study, CZTS NCs were prepared and then decorated with sodium. An increase by almost 50% was seen in the devices which included sodium as compared to those that didn’t and this enhanced performance was explained by larger minority carrier lifetimes and an increase in the carrier concentration which arose due to defect passivation by sodium (Zhou et al., 2013). NaCl treatment to CZTS NC ink based films has also been shown to increase grain size, decrease band gap (from about 1.27 eV to 1.08 eV) and increase absorption coefficient thus proving how this simple treatment can be used to the advantage to further improve the quality of CZTS nanocrystal based devices (Kim et al., 2014).

The current chapter therefore covers each of these areas described above, relevant to the application of CZTS NCs to solar cells and demonstrates the synthesis and optimization of pure CZTS ink followed by the synthesis of CZTS inks with varying S to Se ratios and finally the synthesis of gallium doped CZTS ink. The current study also details devices fabricated using all these inks along with additional surface treatments to the absorber layers (argon annealing, selenization and NaCl treatment) and compares the performance of different inks to arrive at the optimal combination that gives the best device efficiency.
6.2 Experimental techniques

6.2.1 CZTS ink synthesis (standard sample)

Synthesis of the standard CZTS ink was carried out following the stoichiometry: Cu:Zn:Sn:S = 2:1:1:4. The precursors used were copper acetylacetonate (1 mmol), zinc acetate (0.5 mmol), tin chloride = 0.5 mmol and sulphur flakes (2 mmol). All precursors were purchased from Sigma-Aldrich and were >99.99% purity. The precursors were weighed out and put inside a 50 ml three neck flask along with a magnetic stir bar and its necks were sealed with rubber septa. A thermocouple was inserted into one of the necks which would later be connected to the temperature controlled. The flask was then taken into a glove box for adding Oleylamine (OLA) which acts as the solvent, reducing agent and ligand in this reaction. 20 ml of OLA (which had been previously degassed and stored in the glove box), was added to the precursor powders already in the flask using a syringe and the septa was sealed again. This process also allowed for air which would be in the flask to be replaced by the nitrogen which fills the glove box thus getting rid of any oxygen that may spoil the reaction. After this, the flask was taken out of the glove box once more and the thee necks were tied with wire to prevent the septa from bursting out due to build-up of pressure inside the flask during synthesis. Now this flask was attached to the Schlenk line the working of which has been detailed in chapter 2. Before the flask is connected to the line, a vacuum of ~5x10^-4 Torr already exists in one line and nitrogen is flowing through the other. The flask rests in a heating mantle which is connected to a digital temperature controller which maintains the set temperature by monitoring the temperature being input by the thermocouple (immersed in the precursor solution). The heating mantle in turn, rests on a stir plate and the sample is constantly stirred at ~600-800 rpm to allow all the precursor powders to dissolve.

For the first step of the reaction, it is required to degas the OLA to remove any dissolved oxygen that may still be present in it. For doing this, the tap connecting to the vacuum line was opened allowing the solution in the flask to be degassed. At the same time the sample temperature was raised to ~50°C and maintained at this. Degassing was carried out usually for 30 minutes however
this can vary on a sample to sample basis and normally it is carried out until no more visible bubbles can be seen coming out of the OLA solution which indicates that most of the dissolved oxygen has been removed. Once degassing is complete, tap to the vacuum line was closed and at the same time the tap to the nitrogen line was opened allowing this to fill the flask. Now the temperature was raised to 110°C under nitrogen and maintained for 30 minutes allowing all the reactants to completely mix following which the temperature was further raised to 280°C (still under nitrogen) and this was maintained for 60 minutes or whatever reaction time was being studied. This final stage is the one at which the actual reaction is said to be happening. Once the reaction time is up, the solution in the flask is allowed to cool down to room temperature under nitrogen and then finally removed from the line and taken for washing.

Washing of the material is done alternately in ethanol and toluene. First, excess ethanol is added to the solution from the flask which dissolves the impurities and this is centrifuged at 7000 rpm for 3 minutes. The supernatant is thrown away and toluene added to the precipitate left at the bottom of the tube and the tube is shaken well to dissolve all the precipitate in the toluene, followed by centrifugation at 7000 rpm for 3 minutes. This time the supernatant is kept (which contains dissolved nanocrystals) and the precipitate is thrown away. In this step, in addition to unreacted impurities, any poorly capped CZTS nanocrystals will also precipitate out and can be removed. This is again followed by ethanol washing and then the toluene washing. The solution obtained after the second toluene centrifugation is considered to have the pure nanocrystals dispersed in it and this is stored in a vial in a glove box for further characterization. The technique described above is the standard method followed for all ‘standard’ CZTS sample synthesis. The standard sample in this study will be referred to as A4 in the rest of this chapter.

With the aim of studying the effect of synthesis temperature and time variations were made within this process. To study the variation in synthesis time, everything in the sample processing was kept the same except the last stage in which the temperature is raised to 280°C and maintained for 60 minutes. Now, to vary the synthesis temperature, the same reaction was carried out at 220°C, 240°C and 260°C to study any differences that may arise in the sample’s crystallinity, band gap and phase
purity. These samples will be referred to as A1, A2 and A3 for 220°C, 240°C and 260°C respectively for the rest of this chapter.

Similarly, to study the variation in synthesis time, the standard sample was prepared only this time the synthesis stage at 280°C was not maintained for 60 minutes. Instead, as soon as 280°C was reached a timer was started and aliquots were taken out from the sample using a syringe at 5, 10, 15, 30 and 45 minutes and the respective sample names will be A5, A6, A7, A8 and A9 respectively. This allowed the collection of nanocrystals which would show the changing sample quality as the reaction progressed. Each aliquot collected was cleaned following the same ethanol and toluene washing process described earlier and stored for detailed characterization.

6.2.2 CZT(S<sub>1-x</sub>Se<sub>x</sub>) ink synthesis (with x = 0.37 and 0.61)

Synthesis of CZT(S<sub>1-x</sub>Se<sub>x</sub>) inks with varying S and Se ratios was carried out to yield two inks, one in which x was 0.37 (therefore with a larger amount of S) called sample A11 and the second with x = 0.61 (with a larger amount of Se) called sample A10. For this reaction, copper iodide, zinc acetate and tin chloride powders were used as the copper, zinc and tin precursors. 1-Dodecanethiol (DDT) and Diphenyl Diselenide (DPDS) were used as the sulphur and selenium precursors respectively. For sample A10, 0.56 mmol of CuI, 0.7 mmol of Zn(CH<sub>3</sub>COO)<sub>2</sub>.2H<sub>2</sub>O, 0.28 mmol of SnCl<sub>2</sub>.2H<sub>2</sub>O, 1.2 mmol of DDT and 0.56 mmol of DPDS were used. For sample A11, 0.56 mmol of CuI, 0.84 mmol of Zn(CH<sub>3</sub>COO)<sub>2</sub>.2H<sub>2</sub>O, 0.42 mmol of SnCl<sub>2</sub>.2H<sub>2</sub>O, 1.2 mmol of DDT and 0.28 mmol of DPDS were used. The number of mols were varied a little from the standard stoichiometry to account for the different reactivities of different salts. To carry out both these reaction, the precursor powders and DDT were added into a three neck flask with 20 ml of OLA and heated to 180°C under nitrogen (following degassing etc. as described previously). At the same time the DPDS was dissolved in another three neck flask in 10 ml of OLA and filled in a syringe and kept ready for injection. When the first flask (with precursor solution) had reached 180°C, the DPDS was injected into it through its sealed septa. This caused an immediate fall in temperature to ~160°C and now the temperature of this solution was allowed to increase to 280°C which was the final
reaction temperature and maintained for 30 minutes. After this time was up, the flasks were allowed to cool to room temperature and their contents washed as described earlier except hexane was used instead of toluene and centrifugation was carried out at 4000 rpm instead of 8000 rpm for a duration of 1 minute. The final precipitate of nanocrystals was dispersed in hexane and stored for further characterization.

6.2.3 Doped CZTS ink

The synthesis of doped CZTS ink was carried out following the exact same procedure as described for the standard sample in section 6.2.1 however the only difference was that the ratios for the standard sample were Cu:Zn:Sn:S = 2:1:1:4 whereas for the doped sample gallium in the form of gallium acetylacetonate was added such that the ratio was Cu:Zn:Sn:Ga:S = 2:1:0.4:0.6:4. The rest of the synthesis and washing were as described before. This sample will be referred to as A12 in this chapter. Other than these inks described here, a number of other inks were also synthesized however they were part of the optimization process to make the standard ink and have not been described here as either they were not stoichiometrically correct or some problem occurred during the reaction because of which the ink was unusable. Following synthesis and washing, the inks were sprayed onto the desired substrates (Mo coated or Au coated glass) and devices were fabricated. The table including details of all the devices fabricated and tested is given later in this chapter. During device fabrication, various types of treatments were also given to the film including selenization, argon annealing and NaCl treatment and the details of how these were carried out have been described in chapter 2.

6.3 Results and discussion

Figure 6.1 shows the complete characterization of the ‘as-prepared’ (AP) standard CZTS ink of sample A4. As can be seen, the TEM micrograph (parts (a) and (b)) show well-formed nanocrystals (NCs) with minimal agglomeration and an approximate nanocrystal diameter of 25nm. The images also show that there are no visible impurities within the NCs implying that the washing process was successful in removing unreacted material and poorly capped NCs.
The x-ray diffractogram in part (c) has been indexed using the standard JCPDS database (card number 260575) and shows clearly the main peaks corresponding to Kesterite CZTS including (112), (220) and (312). The sharp nature of these peaks and lack of other secondary phases proves the phase purity of the sample. However, since all secondary phases may not always show up in x-ray diffraction data, Raman spectroscopy was carried out on the sample and part (e) of figure 6.1 shows the resultant data. In this a sharp A1 mode peak at ~336 cm⁻¹ (marked with the black dashed line) is clearly present which further confirms the formation of Kesterite CZTS and a lack or minimal presence of secondary phases. UV-Visible spectroscopy was carried out on the samples and part (d) of figure 6.1 shows the data for this. From the absorbance curve it can be seen that the band edge position lies at ~1.2 eV. The absence of sub-bandgap absorption also corroborates the theory that there are no unwanted secondary phases present in the sample. Finally to confirm that the stoichiometry of the sample was correct, EDAX analysis was carried out which established the atomic percentages of Cu, Zn, Sn and S (normalized with respect to Sn) to be 1.89, 0.98, 1 and 3.83 respectively which match very closely with the standard values of 2, 1, 1, and 4 for CZTS.
Figure 6.2 TEM images for samples A1 to A4 prepared at 220°C, 240°C, 260°C and 280°C respectively.
Once this standard sample had been optimized, temperature variation was carried out as described earlier and samples A1, A2 and A3 were prepared at 220°C, 240°C and 260°C respectively. The TEM images for these samples along with those of A4 (for comparison) can be seen in figure 6.2 and the x-ray diffraction and absorbance data is shown in figure 6.3. Figure 6.2 parts (a) to (h) clearly show how the quality of the NC ink changes as synthesis temperature increases. At 220°C, it is seen that the crystalline quality is poor which improves significantly as the temperature is raised to 240°C and then 260°C. Finally at 280°C (standard sample) it can be seen that the number of NCs has increased greatly as has their average size which is very important from the point of view of device application. The same trend can be seen in the x-ray diffraction data in part (a) of figure 6.3. This shows that as the synthesis temperature increases, the number of peaks corresponding to Kesterite CZTS goes up and the height of the peaks also increases indicating the formation of a larger number of NCs with pure Kesterite phase. The absorbance data in part (b) of the figure shows that as the synthesis temperature increases, the band edge position decreases from ~1.4 eV to ~1.2 eV which can be attributed to the formation of the correct phase of CZTS.

Figure 6.4 shows the TEM micrographs for samples A5 to A9 which were taken out as aliquots at 5, 10, 15, 30 and 45 minutes of a ‘standard’ CZTS reaction. From the images it can be seen that at the 5 minute mark, the NCs have a very non-uniform size distribution and on the on the whole they are poorly formed. As time passes it can be seen that at 10 minutes and then 15 minutes, their size distribution improves a lot and the NCs are quite homogenous.

![Figure 6.3 (a) X-ray diffraction and (b) absorbance data for samples A1, A2 and A3 prepared at 220°C, 240°C and 260°C respectively](image-url)
Figure 6.4 (a) to (l) show TEM images for samples A5 to A9 with synthesis times of 5, 10, 15, 30 and 45 minutes respectively. Parts (i) and (l) show sample A4 made for 60 minutes for comparison.
As the ink is allowed to react for more time, it’s seen that the size of the NCs increases with very little difference between the 45 and 60 minute samples.

Figure 6.5 shows the x-ray diffraction data for these samples. As we move up from A5 to A9 (and A4 on the top for comparison), it can be seen that the diffraction peaks corresponding to Kesterite CZTS planes at (112), (220) and (312) become sharper and narrower and there is the emergence of the peak corresponding to (332) in A4 at 60 minutes synthesis time. This shows that as synthesis time increases, secondary phases such as CuS and ZnS which may be reflected in the shoulder peaks present in the (112) CZTS peak go down probably because of complete dissociation and reaction of the precursors and at 60 minutes synthesis time, the peaks are sharp and well-defined and correspond only to pure CZTS (as has also been confirmed by Raman spectroscopy previously). The absorbance data for these samples also shows that as synthesis time increases the band edge energy decreases which also points towards formation of kesterite CZTS with minimal secondary phases.

For samples A10 and A11, where S and Se ratios were varied during synthesis, the TEM images are shown below in figure 6.6. As it can be seen that the shape of these NCs, particularly those for A11 are slightly different from what was seen in all the earlier samples. Such NCs are said to be ‘rice grain’ shaped and it has been previously reported that such a shape can actually enhance device performance by increasing sample conductivity (Li et al., 2012). In the case of A10 it can be seen
that the NCs density is much lower compared to A11 and other previous inks. Since A10 has $x = 0.61$ therefore this sample can be said to be ‘more CZTSe like’ and A11 with $x = 0.37$ can be said to be ‘more CZTS like’. Figure 6.7 shows XRD, Raman and absorbance data for both these samples. As can be seen, the peaks in the x-ray diffraction spectrum do not look like the any of the previous spectra for Kesterite CZTS and this is because this particular reaction yields Wurtzite CZTS. The peaks for A10 and A11 are a mixture between Wurtzite CZTS and CZTSe and the intensities vary depending on the concentration of S and Se in the sample. However it is very difficult to assign individual peaks to CZTS and CZTSe because they are largely overlapping, still, it can be said that in sample A10, the peaks beyond 60° are due to Wurtzite CZTSe which is to be expected as this sample is more ‘CZTSe like’. The explanation behind the emergence of this particular phase in these samples can be based on the fact that OLA was used as the solvent and the selenium precursor was DPDS. It has been previously shown (Wang et al., 2012) that in samples where both of these were used, CZTSe was preferentially formed in its Wurtzite phase.

![Figure 6.6 TEM images for samples A10 and A11 with varying S and Se ratios](image)

*Figure 6.6 TEM images for samples A10 and A11 with varying S and Se ratios*
Raman spectroscopy of the two samples also exhibited peaks corresponding to both CZTS and CZTSe. In part (a) of figure 6.7, the high, sharp peak at ~191.2 cm\(^{-1}\) corresponds to CZTSe and similarly in part (b), the clear peak at ~331 cm\(^{-1}\) matches CZTS. However, in (a) peaks for CZTS are also visible at ~330 cm\(^{-1}\) and in (b) peaks for CZTSe are present at ~187 cm\(^{-1}\) thus proving formation of both phases in the A10 and A11. Finally parts (e) and (f) show the absorbance edges for A10 and A11 to be at ~1.09 eV and 1.4 eV respectively which match well with the values expected for the higher Se and S ratios. It is anticipated that as S or Se is increased by a large amount in either sample, the characteristic peaks in XRD and Raman data will move even more towards CZTS and CZTSe respectively. However, a negative point observed in these samples was the yield was very low as compared to the standard CZTS ink prepared and therefore not very cost effective.

The final ink synthesized in this study was doped CZTS and this is a novel ink prepared for the first time in this study. Previously, studies have reported a marked improvement in efficiencies of CZTS nanocrystals by doping them with germanium (Guo, et al., 2012).
It has also been suggested from first principle calculations that in CZTS and CZTSe, the CBM (conduction band minimum) has antibonding s as well as p (anion) hybrid orbitals. Similarly the VBM (valence band maximum) has mostly hybridizations of the p (anion) and Cu d type orbitals. Now like germanium, gallium has a smaller atomic radii than tin, and when it is used to replace tin in the lattice these smaller gallium atoms would cause the s-p and s-s repulsion to strengthen between the gallium and the sulphur (in this case) which should cause an increase in the antibonding CBM. This in turn should cause an increase in the band gap of the alloyed CZTS (a-CZTS). Also, since the larger tin atoms are getting replaced by smaller gallium atoms theoretically this should lead to a slight unit cell contraction, there should also be a slight shift towards a higher 2-theta value in the x-ray diffractogram for the a-CZTS as compared to standard CZTS. The complete characterization data for this is shown in figure 6.8. Part (a) shows the TEM image showing a
Ink Back contact + no. of passes Ar annealing of absorber layer Additional treatment Jsc (mA/cm²) Voc (V) FF η (%) (υ)

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<th>Ink</th>
<th>A4</th>
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<td>Mo(4p)</td>
<td>0.001</td>
<td>0.003</td>
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<td>Mo(8p)</td>
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<td>Selanization</td>
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Table 6.1. Comparison of device characteristics for A4 and A12 (Mo(2p), (4p) and (8p) refers to molybdenum coated glass substrate on which 2, 4 and 8 passes were made during the spraying, therefore an increasing number of layer and consequently thickness.
some-what lower NC density as compared to the standard CZTS ink. This fact can also be seen in figure 6.9 where the picture showing the actual NCs dispersed in toluene shows clearly that A4 (as prepared) is of much higher concentration than A12 (as prepared). Calculations showed the concentration of A4 to be approximately two times that of A12 and therefore in later sections when devices are made with these inks, to facilitate accurate comparison, the thickness of layers made of A12 were kept twice that of A4 for all cases. Part (b) of figure 6.8 shows the absorbance data and it can be seen that the absorption edge is shifted to higher energy from the typical value for CZTS (~1.2 eV) and is ~1.6-1.65 eV. This is in accordance with the explanation given earlier for a-CZTS.

Part (c) shows the Raman spectra for the sample and the characteristic peak near 330 cm\(^{-1}\) is present. Finally part (d) shows the x-ray diffraction data. The sharp peaks at 38.1°, 40.5° and 73.4° correspond to Mo which was the substrate onto which the film was sprayed before carrying out XRD. The rest of the peaks correspond to CZTS and a slight shifting to a higher value from the standard 2-theta values is seen in the case of the peaks at 44.5°, 48.0°, 56.9° and 64.6° which again is as predicted because of replacement with a smaller atom in the lattice.

All the inks described in this section were sprayed onto substrates of molybdenum or gold, a CdS layer was added by the CBD technique, and top contacts of ZnO and ITO were deposited by sputtering (as described in chapter 2). Different conditioning treatments were also given to the device at different stages in its assembly and these were: (i) argon annealing of the absorber layer (CZTS) at 300°C, (ii) air annealing of the absorber layer at 300°C, (iii) argon annealing after CdS deposition at 500°C, (iv) selenization of absorber layer and (v) NaCl treatment of absorber layer.

The characteristics measured for all the devices made are not given here as there were 100+ devices and most of them gave very low or no efficiency because for the most part this study was based on the optimization procedure. However the most important results were from samples 4 and 12 and these are shown in table 6.1. Since A12 was approximately half the density of A4, therefore for a fair comparison, double the number of “passes” or coatings were made for A12. Therefore, 2 passes of A4 are comparable to 4 of A12 and 4 of A4 are compared to 8 of A12.
Figure 6.9 (a) and (b) show 3D topography of A4 and A12 respectively, (c) and (d) are histograms showing the average surface potential distribution for A12 and A4 respectively.
6.3 Conclusions

In the present study, the synthesis of stoichiometrically correct CZTS nanocrystalline ink was optimized. Synthesis temperatures were varied and 280°C was found to be the optimal temperature for the growth of large, good quality nanocrystals which exhibited a pure Kesterite phase and the band gap decreases to 1.2 eV. The effect of synthesis time on nanocrystal quality was studied by taking aliquots of the standard sample being synthesized at 280°C at intervals of 5, 10, 15, 30 and 45 minutes after start of the reaction. The characterization of these aliquots proves that as synthesis time increases, the crystalline phase moves towards Kesterite CZTS and the size distribution becomes more homogenous. The fact that there was not much noticeable difference between the 45 minute and 60 minute aliquot in terms of crystal size but the XRD spectra for the 60 minute sample has the narrowest and sharpest proves that 60 minutes was the optimal growth time. Thus growth parameters for the standard sample were established and EDAX analysis proved the ratio of Cu:Zn:Sn:S to be ~2:1:1:4 which matches the ideal stoichiometric values for CZTS.

Samples with atomic ratios CZT(S_{1-x}Se_x) with x = 0.37 (A11) and 0.61 (A10) were synthesized to give ‘CZTS-like’ and ‘CZTSe-like’ samples and the corresponding, Raman and XRD spectra both show properties of CZTS and CZTSe with a very low band gap of ~1.09 eV and 1.4 eV respectively. The synthesis of such CZTSSe NCs can allow the incorporation of the benefits of selenization without having to carry out post-synthesis, high temperature processing. Finally, doped CZTS ink with gallium partially replacing tin in the lattice structure was synthesized which to the best of our knowledge is the first report of its kind. This ink showed an increased band gap of ~1.65 eV as well as a slight shift to higher 2-theta values in the XRD spectra, both of which prove that tin has indeed been replaced by the smaller atom of gallium in the CZTS structure.

To be able to actually compare the functionality of the inks, devices were formed and tested and the effect of different conditioning treatments was studied. The results clearly demonstrated the superior performance of the doped CZTS ink (A12) over the standard ink (A4) for every condition tested. This can be explained by the effect the gallium doping has on the lattice structure and bond
formation as explained in the previous section. Also to try and understand this further, Kelvin probe force microscopy was carried out for A12 and A4 and the resulting histograms showing surface potential distribution for each in the dark is shown in figure 6.9 (c) and (d). This shows that A12 has a surface potential almost ~270 mV higher than that of A4 and therefore a higher work function. Therefore A12 will have an overall higher density of holes as compared to A4 and this will finally be reflected in terms of an enhanced Voc. The fact that as seen in table 6.1, the Voc for devices made by using A12 is higher than that of the devices made from A4 for every case, proves this theory. Thus the novel gallium doped ink developed in this study has great potential for solar cell application.