

# Chapter 3

## Deposition technology: Chemical closed- space vapor transport (CCSVT)

The need for high quality CuGaSe<sub>2</sub> thin films materials of reproducible reliability and characteristics has driven films growth technology through a rapid succession of significant achievements. CuGaSe<sub>2</sub> is one of the most promising wide- gap chalcopyrite absorbers for polycrystalline thin-film solar cells. Many easily scalable and high throughput techniques for CuGaSe<sub>2</sub> semiconductor film growth have been developed in the past ten years with the potential to yield high efficiency based on certain criteria such as:

- Material yield
- Source stability
- Control of the film uniformity and stoichiometry
- Reproducibility of film parameters
- Ability of fine tuning of the composition and electronic properties
- Equipment cost

Considering these criteria, a novel efficient growth technique called chemical closed- space vapor transport (CCSVT) technique [44] at moderate source and substrate temperatures for chalcopyrites deposition, has been implemented. Keeping in mind that the understanding of the complex issues between the film properties and how they are affected by processing is a challenge, this chapter provides an investigation of the CCSVT process variables to establish processing- structure property relationships. In the section 3.1 we present a description of the new CCSVT method used for the deposition of single phase CuGaSe<sub>2</sub> thin films. A description of the deposition technique used for chalcopyrite fabrication is presented and section 3.2 deals with the monitoring steps of the chalcopyrite film parameters and structure during growth.

### 3.1 Chemical closed- space vapor transport (CCSVT)

The processing method is relevant for the growth of high quality and large area CuGaSe<sub>2</sub> thin films, which in turn are very important for device applications. The growth of CuGaSe<sub>2</sub> films have been realized by various deposition techniques. CuGaSe<sub>2</sub> single crystals grown

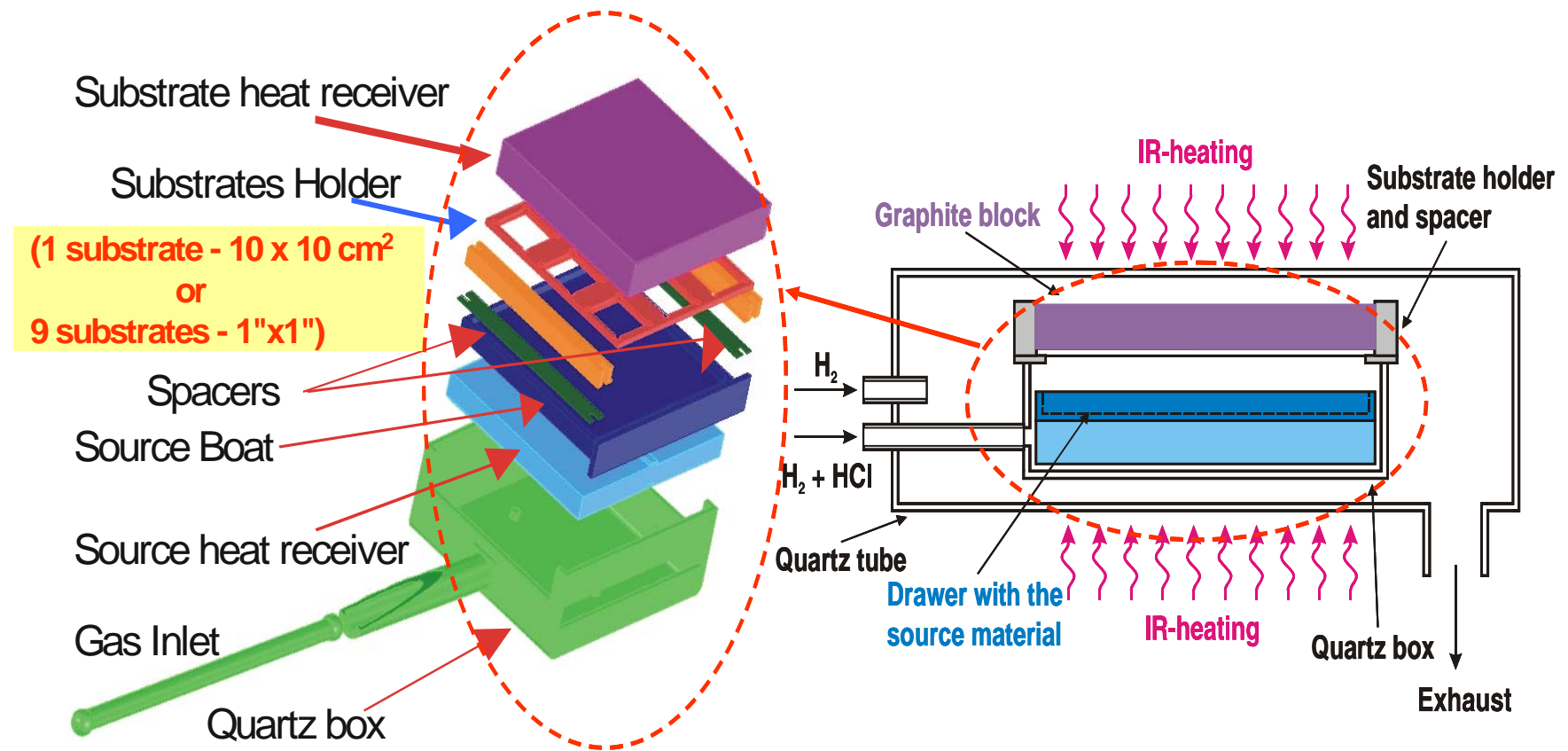
by chemical vapor transport (CVT) in a closed system have reached efficiencies of 9.7% [45] while 9.3% [46] efficient solar cells were prepared by using polycrystalline  $\text{CuGaSe}_2$  thin films grown by physical vapor deposition (PVD). Usually, high quality  $\text{CuGaSe}_2$  absorber thin films are prepared by PVD [47, 48], or molecular beam deposition [49]. However, these techniques apply high temperatures for the source material evaporation (above  $1000^\circ\text{C}$ ). This constitutes the major hurdle for industrial upscaling. The costs of the  $\text{CuGaSe}_2$  film preparation can significantly be decreased by:

- Taking advantage of the CVT [45, 50] and closed -space vapor transport (CSVT) [51, 52, 53] techniques, namely, fast volatilization of source materials by reaction with halogens such as molecular  $\text{I}_2$ ,  $\text{Cl}_2$  or  $\text{HCl}$  to gaseous halogenides which occurs at significantly lower temperatures,
- Using III-VI compounds exhibiting low sublimation temperatures in combination with copper-selenides and -sulfides [54, 55], and also
- Employing advantages of the rapid thermal processing (RTP) [56], thermal annealing of the metal precursors deposited on large areas.

Motivated by the limitations of the above mentioned techniques, an alternative deposition technology based on the advantages of these techniques was developed. The new chemical closed- space vapor transport (CCSVT) technique [57], with flexibility and high control of the technological parameters as the main priorities for the deposition of high quality binary and multinary compounds at moderate source and substrate temperatures was chosen for this work.

### 3.1.1 CCSVT apparatus

A schematic drawing of the CCSVT system is shown in figure 3.1. A graphite CCSVT reaction cell is placed in a quartz box which has an inlet tube for the gaseous transport agents, ( $\text{I}_2$ ,  $\text{HCl}$ ), used for volatilization of the  $\text{Ga}_2\text{Se}_3$  source material. A spacer is used for the adjustment of the distance between source drawer and substrate holder, where one  $10 \times 10 \text{ cm}^2$  substrate or 9 inch by inch substrates can be mounted. The source material in the form of fine grained powder fills the source drawer, which allows easy refilling. The complete CCSVT quartz box is placed in a quartz tube which can be evacuated or filled with gas. The substrate holder and the drawer with the source material, which are the substrate and source susceptors, are made from purified high- density graphite. Arrayed infrared units (12 units - 1000 W per unit) are used as heaters for the source drawer and the substrate independently of each other. The temperature is controlled by thermocouples at the source and substrate sides and can be set independently.

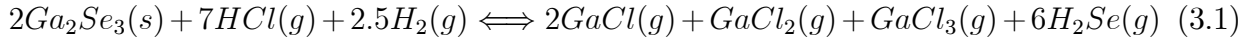


**Figure 3.1.** Basic features of the chemical closed- space vapor transport (CCSVT) system used to grow  $\text{CuGaSe}_2$  thin films.

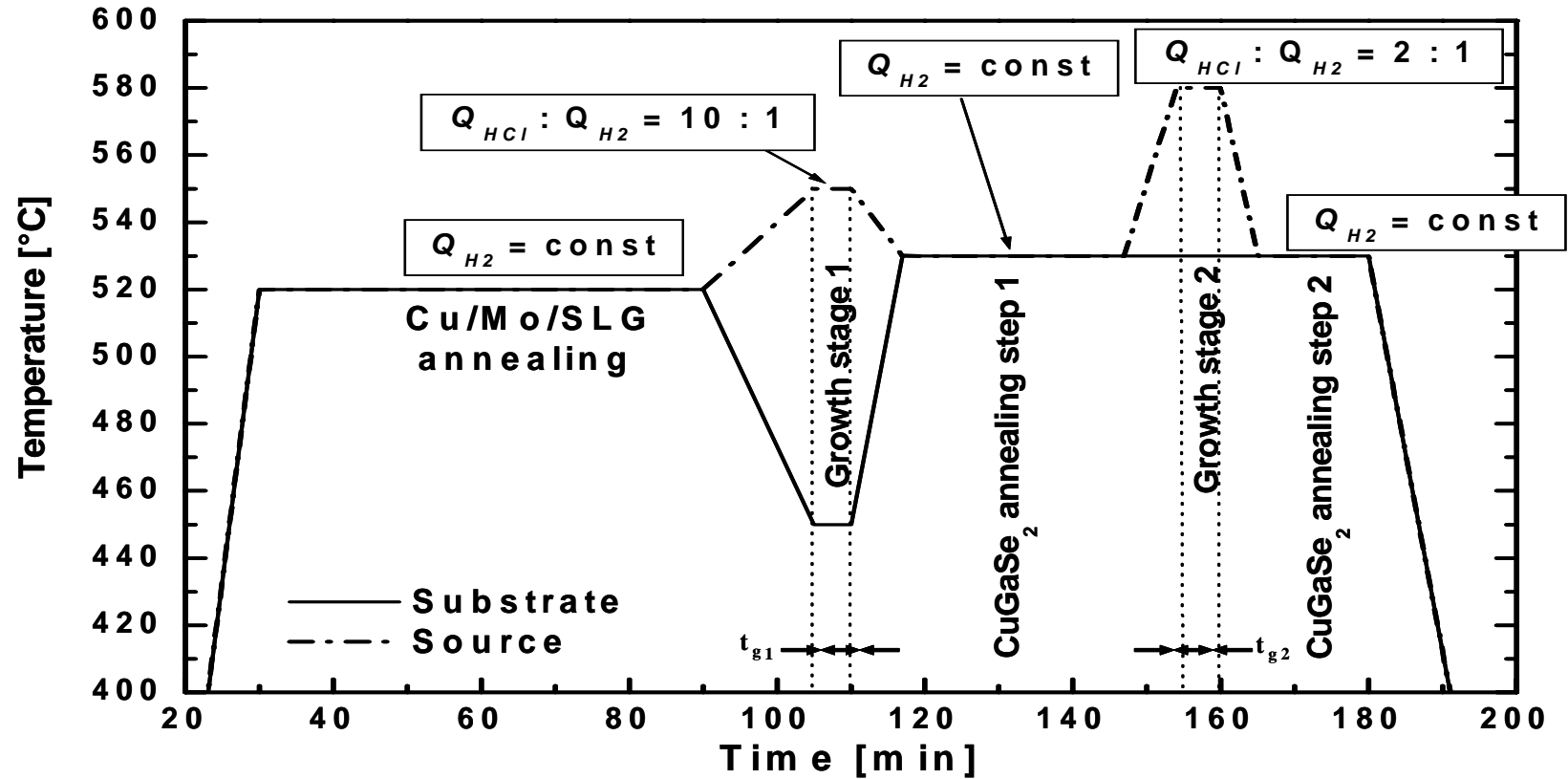
### 3.1.2 CuGaSe<sub>2</sub> film growth by CCSVT

The starting material is the Ga<sub>2</sub>Se<sub>3</sub> powder source material synthesized from 6N pure elements placed in a drawer which allows easy changing of the source material. The growth process of CuGaSe<sub>2</sub> films was investigated by systematic variation of the following parameters: the source temperature ( $T_{source}$ ); the substrate temperature ( $T_{substrate}$ ); the distance between the source and the substrate holder ( $d_{source-substrate}$ ); the reactor pressure ( $P_{reactor}$ ); and the gaseous HCl content within the H<sub>2</sub> carrier gas ( $Q_{HCl} : Q_{H_2}$ ), where  $Q_{HCl}$  and  $Q_{H_2}$  are quantities of HCl and H<sub>2</sub> gas, respectively. These parameters fell within the following ranges:  $T_{source} = 520 - 580^\circ C$ ;  $T_{substrate} = 420 - 480^\circ C$ ,  $d_{source-substrate} = 8 - 18$  mm;  $P_{reactor} = 300$  mbar up to 800 mbar and  $Q_{HCl} : Q_{H_2} = 2:1 - 10:1$ . Gaseous HCl diluted by H<sub>2</sub> gas is used as transport agent, while additional hydrogen serves as buffer gas in the quartz tube which surrounds the reaction cell. HCl and H<sub>2</sub> gas quantities,  $Q_{HCl}$  and  $Q_{H_2}$ , respectively are externally controlled by mass-flow meters.

Substrates consisting of 250 nm thick Cu films evaporated on clean or Mo- coated (Mo thickness of  $\sim 750$  nm) soda lime glass (SLG) were used for CuGaSe<sub>2</sub> growth. CuGaSe<sub>2</sub> thin films are prepared by annealing the Cu precursors deposited on clean or Mo- coated soda lime glass (SLG) substrates under gaseous GaCl<sub>x</sub>/H<sub>2</sub>Se atmosphere in the CCSVT system. The Ga<sub>2</sub>Se<sub>3</sub> employed as source material is stoichiometrically volatilized by a controlled amount of HCl/H<sub>2</sub> agent at a certain pressure. The reaction between solid Ga<sub>2</sub>Se<sub>3</sub> and HCl and H<sub>2</sub> occurs in the equilibrium state at high H<sub>2</sub> to HCl ratio (HCl : H<sub>2</sub> > 1 Mol : 50 Mol) and the corresponding reaction is expressed by the chemical equation 3.1:



where  $g$  and  $s$  denote the gaseous and solid state, respectively. In figure 3.2 all steps for the CuGaSe<sub>2</sub> preparation are displayed.



**Figure 3.2.** Source and substrate temperature as a function of process time including all steps in the  $\text{CuGaSe}_2$  thin film growth by CCSVT.  $Q_{H_2}$  and  $Q_{HCl}$  are  $H_2$  and  $HCl$  quantities, respectively.

- In the preliminary step, the source temperature ( $T_{source}$ ) and substrate temperature ( $T_{substrate}$ ) are increased simultaneously up to 520°C at a constant hydrogen flow.
- In the second step, at 520° C, the Cu- rich surface of the Cu/Mo/CuGaSe<sub>2</sub> structure is cleaned in-situ from copper oxides by reaction with hydrogen. It is also used for the preliminary Na diffusion through the Mo film towards Mo/Cu interface. This step is called ‘substrate annealing’ and lasts one hour.
- During the third step called ‘growth stage 1’ - (GS-1), source and substrate temperatures are adjusted to 550°C and 450°C, respectively and the  $Q_{HCl} : Q_{H_2}$ -ratio to 10:1. Cu from the substrate reacts with the volatilized gas phase compounds of Ga<sub>2</sub>Se<sub>3</sub>, GaCl, GaCl<sub>2</sub>, GaCl<sub>3</sub> and H<sub>2</sub>Se (equation 3.1) and CuGaSe<sub>2</sub> grows. However, the process reproducibility was poor, resulting in different film thicknesses and compositions for the same ‘growth stage 1’ time,  $t_{g1}$ . Moreover, deposited CuGaSe<sub>2</sub> sometimes contained Cu<sub>2</sub>Se phases although the film composition was Ga- rich. Therefore, in further experiments the time  $t_{g1}$  was adjusted for the preparation of Cu- rich CuGaSe<sub>2</sub> thin films. At the end of this stage, Cu- rich CuGaSe<sub>2</sub> films are grown at a deposition rate of 230 - 240 nm/min.
- Fourth step: after stopping the HCl input flow, the third step was then followed by CuGaSe<sub>2</sub> annealing at an annealing temperature of 530°C, which is the melting point of CuSe [58]. Hence, liquid CuSe together with Cu<sub>2-x</sub>Se species that are in quasi- liquid state at this temperature [59] serve as solvents for the Ga<sub>2</sub>Se<sub>3</sub> and CuGaSe<sub>2</sub>, improving the crystalline quality of the growing CuGaSe<sub>2</sub> grains.
- During the fifth step, called ‘growth stage 2’ - (GS-2), the fine tuning of the CuGaSe<sub>2</sub> film thickness and composition is realized by increasing the source temperature,  $T_{source}$  up to 580°C and adjusting the  $Q_{HCl} : Q_{H_2}$ - ratio to 2:1. The second growth stage was carried out to dissolve the remaining Cu<sub>2-x</sub>Se phases at a lower CuGaSe<sub>2</sub> deposition rate of 10 to 60 nm/min. The CuGaSe<sub>2</sub> growth rate is significantly reduced, due to reduced HCl content in the H<sub>2</sub> flux and, correspondingly, lower Ga<sub>2</sub>Se<sub>3</sub>, GaCl, GaCl<sub>2</sub>, GaCl<sub>3</sub> and H<sub>2</sub>Se concentrations, and also because of the smaller temperature difference between source and substrate, compared to the temperature difference during the ‘growth stage 1’ - (GS-1).
- Sixth step: after the second growth stage ‘growth stage 2’, an annealing step labelled ‘CuGaSe<sub>2</sub> annealing step 2’ is used at 530°C for film homogenization in the presence of only H<sub>2</sub> buffer gas, while the reactor pressure is maintained constant at 800 mbar.
- After the last step, the reactor is cooled down at a rate of ~13°C/min in the H<sub>2</sub> atmosphere.

Single phase CuGaSe<sub>2</sub> absorber thin films with thickness ranging from 1.5 to 1.9  $\mu\text{m}$  with corresponding  $[\text{Ga}]/[\text{Cu}]$  ratio in the range 1.0 - 1.3 were grown on clean or Mo/SLG substrates. A two stage deposition process is applied for the preparation of the CuGaSe<sub>2</sub> thin films with a required  $[\text{Ga}]/[\text{Cu}]$  ratio. All the parameters of the CCSVT CuGaSe<sub>2</sub> film depositions with the corresponding thickness and composition are summarized in table 3.1.

**Table 3.1** : Survey of the  $\text{CuGaSe}_2$  films prepared by the CCSVT deposition technique with their corresponding deposition parameters, final composition and thickness .

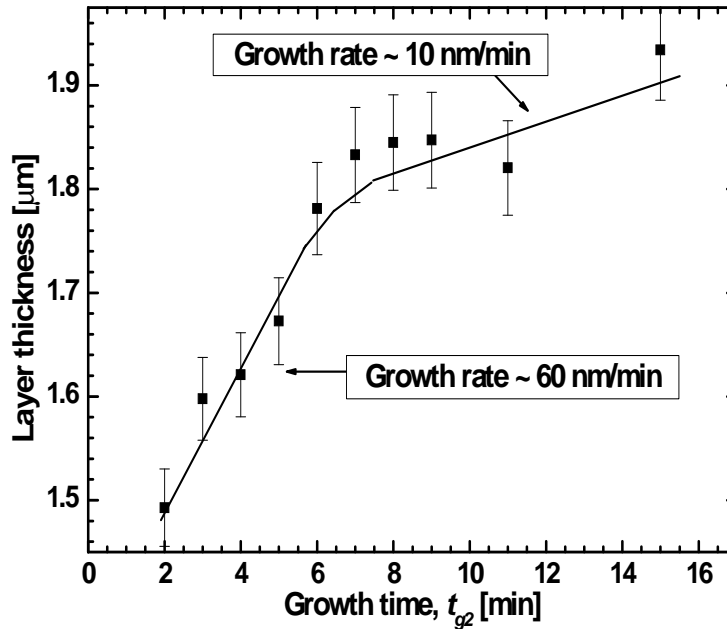
Sample	Growth stage 1 (GS1)				Growth stage 2 (GS2)				Final film properties	
	$T_{source}$ [°C]	$T_{substrate}$ [°C]	Deposition time $t_{g1}$ [min]	Growth rate [nm/min]	$T_{source}$ [°C]	$T_{substrate}$ [°C]	Deposition time $t_{g2}$ [min]	Growth rate [nm/min]	Thickness [ $\mu\text{m}$ ]	[Ga]/[Cu]
1	550	450	5	240	580	530	2	60	1.49	0.86
2	550	450	5	240	580	530	3	60	1.60	0.96
3	550	450	5	240	580	530	4	60	1.62	1.04
4	550	450	5	240	580	530	5	60	1.67	1.07
5	550	450	5	240	580	530	6	60	1.78	1.10
6	550	450	5	240	580	530	7	10	1.83	1.11
7	550	450	5	240	580	530	8	10	1.84	1.14
8	550	450	5	240	580	530	9	10	1.85	1.18
9	550	450	5	240	580	530	11	10	1.82	1.23
10	550	450	5	240	580	530	15	10	1.93	1.29

## 3.2 Influence of the growth conditions on the $\text{CuGaSe}_2$ film properties.

This section is devoted to the evolution of the microstructures in polycrystalline films, resulting in the fine tuning of the  $\text{CuGaSe}_2$  absorber composition which results in a precise control of the absorber properties. Indeed,  $\text{CuGaSe}_2$  films are deposited in the stage GS-1 in Cu- rich conditions resulting in  $\text{CuGaSe}_2$  films containing  $\text{Cu}_2\text{Se}$ . A second growth stage was implemented to dissolve  $\text{Cu}_2\text{Se}$  phases and to allow the fine adjustment of the appropriate  $\text{CuGaSe}_2$  composition and electronic properties.

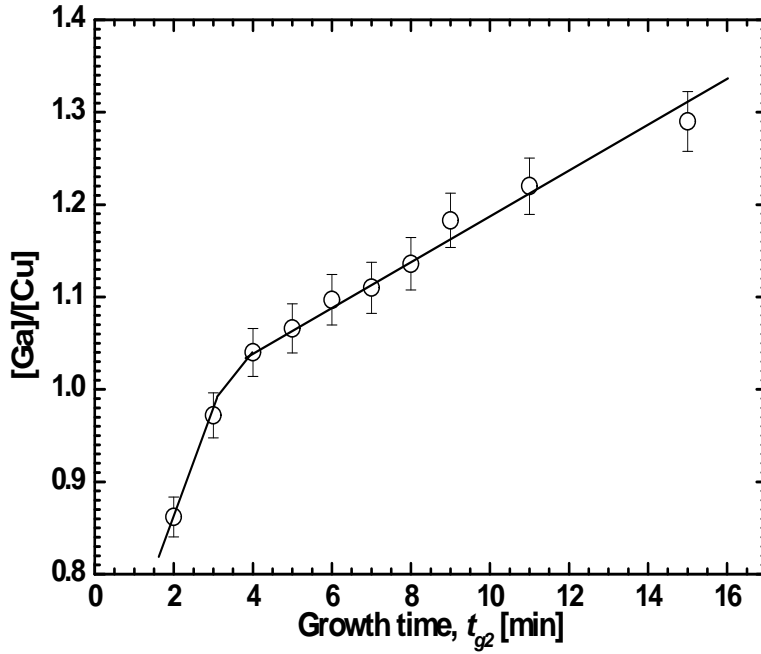
### 3.2.1 Evolution of $\text{CuGaSe}_2$ film thickness, composition, and structure.

Thickness, composition and structure of  $\text{CuGaSe}_2$  films determined by X-ray fluorescence analysis (XRF), elastic recoil detection analysis (ERDA) methods, as well as X- ray diffraction (XRD) spectra were investigated in order to investigate how the second growth stage ‘GS-2’ influences the film properties. Figure 3 3 (a) and Figure 3.3 (b) illustrate the related growth stage 2 time,  $t_{g2}$ , and the film thickness and composition ( $[\text{Ga}]/[\text{Cu}]$  ratio.



(a)

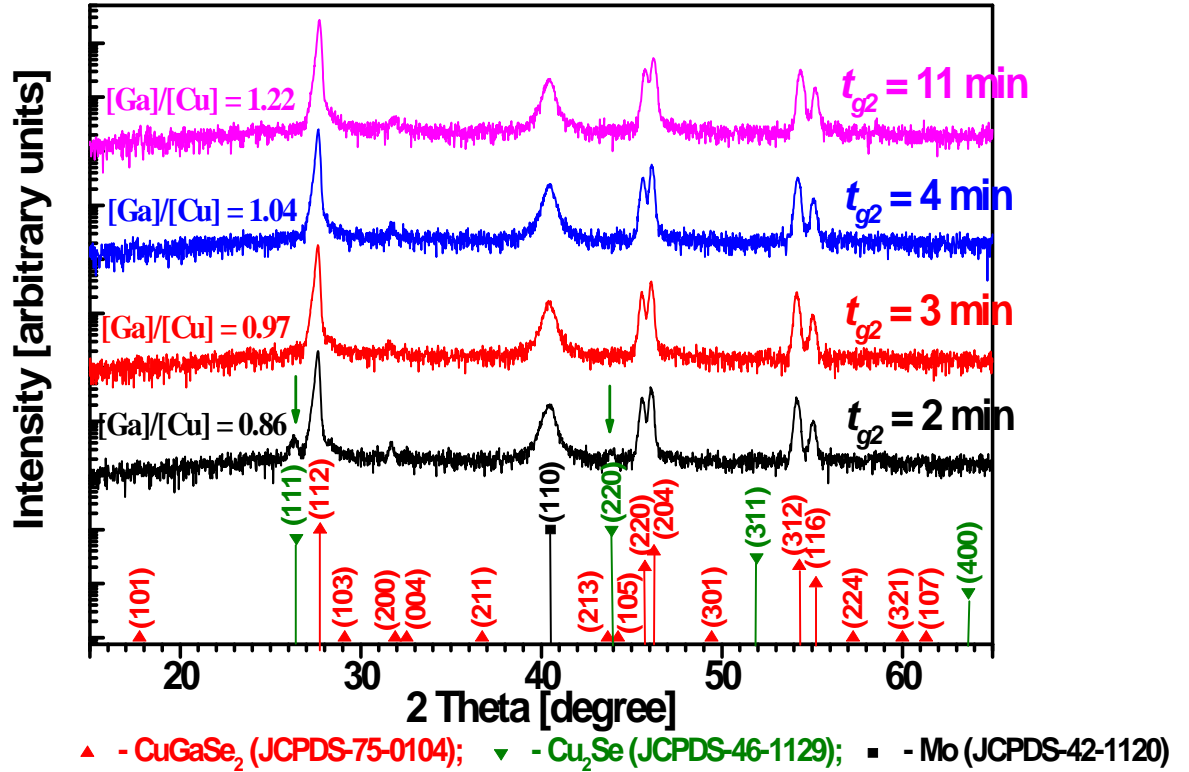




(b)

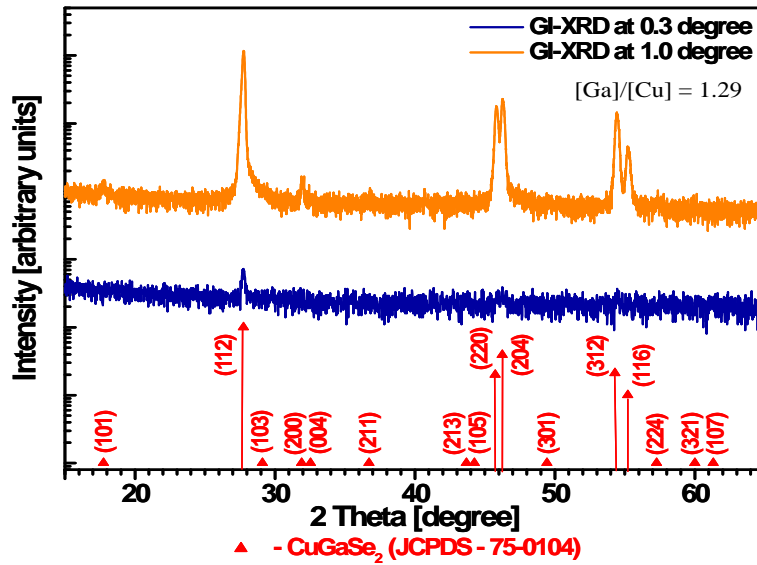
**Figure 3.3.** The evolution of  $\text{CuGaSe}_2$  (a) film thickness and (b)  $[\text{Ga}]/[\text{Cu}]$  ratio as a function of growth time,  $t_{g2}$ , in the second stage of the CCSVT process.

In figures 3.3 (a) and (b) the starting points are  $\text{CuGaSe}_2$  films containing  $\text{Cu}_2\text{Se}$  grown after the first growth stage and subsequently annealed (fourth step in figure 3.2), and having a determined composition and thickness. In the first minutes of the growth stage 2 (GS-2),  $\text{CuGaSe}_2$  films continue to grow with a growth rate of  $\sim 60$  nm/min due to transformation into  $\text{CuGaSe}_2$  of the remaining  $\text{Cu}_2\text{Se}$  phase after the growth stage 1 (GS-1). After  $\text{CuGaSe}_2$  stoichiometry is achieved, the  $[\text{Ga}]/[\text{Cu}]$  ratio continues to increase linearly with  $t_{g2}$ , but with a smaller slope (see Figure 3.3 (b)). Further increase of the  $\text{CuGaSe}_2$  thickness is limited to  $\sim 10$  nm/min and is ascribed to an increased  $\text{CuGaSe}_2$  grain size with increasing Ga content. All these parameters are controlled by the CCSVT process within an accuracy of  $\sim 2.5\%$ . In figure 3.4, XRD spectra as a function of the growth stage 2 time,  $t_{g2}$ , are presented. Several diffraction peaks of  $\text{CuGaSe}_2$  (JCPDS-75-0104),  $\text{Cu}_2\text{Se}$  (JCPDS-46-1129) and Mo (JCPDS-42-1120) can be observed.



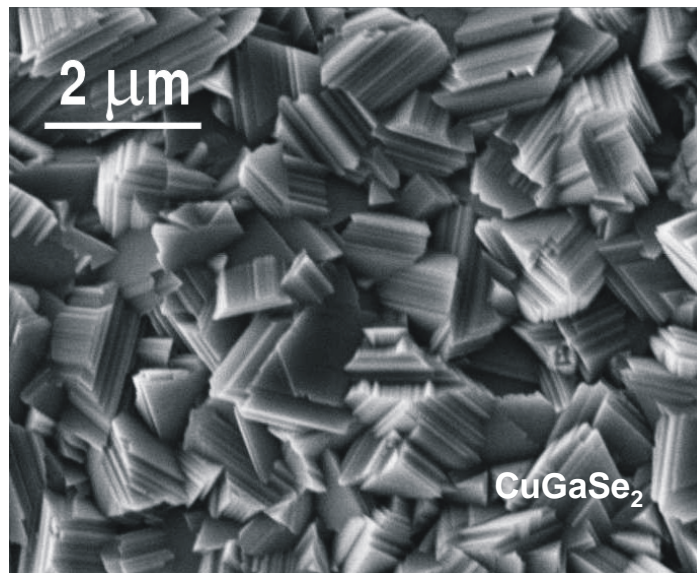
**Figure 3.4.** XRD diffractograms of the  $\text{CuGaSe}_2$  thin films grown on Mo/SLG substrates as a function of the growth time  $t_{g2}$  in the second CCSVT stage. All other process parameters are kept constant, as indicated in Figure 2. The lines and symbols mark the  $\text{CuGaSe}_2$ ,  $\text{Cu}_2\text{Se}$  and Mo reference peak positions according to JCPDS data.

According to the XRD spectra, during the first minutes of the growth stage 2 (GS-2),  $\text{Cu}_2\text{Se}$  phase can still be detected because of the transformation into  $\text{CuGaSe}_2$  of the remaining  $\text{Cu}_2\text{Se}$  phase after the growth stage 1 (GS-1). After about 3 min up to 11 min of growth stage 2 (GS-2),  $\text{Cu}_2\text{Se}$  is not further detected by XRD and only peaks corresponding to the tetragonal (chalcopyrite) crystal structure are recorded in the XRD spectrum. In order to determine whether additional phases such as  $\text{Ga}_2\text{Se}_3$  occurring in general for the films having the composition beyond 112 (stoichiometry), grazing- incidence XRD (GI- XRD) measurements were carried out on the film with a composition 1.29 and corresponding to a second growth time of 15 min (table 3.1).

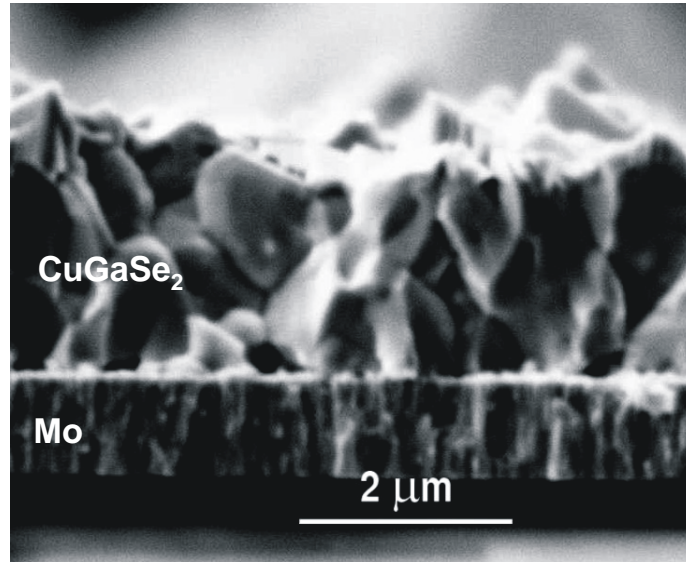


**Figure 3.5 :** GI- XRD measurements performed at incident angles of  $1^\circ$  and  $0.3^\circ$  for a Ga- rich film grown with a second growth time,  $t_{g2}$ , of 15 min. The lines and symbols mark the  $\text{CuGaSe}_2$  peak positions according to JCPDS data.

Figure 3.5 displays the grazing- incidence XRD spectra for the  $\text{CuGaSe}_2$  films prepared with  $[\text{Ga}]/[\text{Cu}]$  ratios of up to 1.29 at incident angles of  $1^\circ$  and  $0.3^\circ$ . It is clearly noticeable that no additional phase such as  $\text{Ga}_2\text{Se}_3$  phase, generally observed for Ga-rich  $\text{CuGaSe}_2$  compounds [60], is observed neither in the  $\text{CuGaSe}_2$  bulk nor on the film surface.  $\text{CuGaSe}_2$  film surface morphology and cross-section images are presented in figure 3.6-(a) and (b), respectively.



(a)



(b)

**Figure 3.6.** Top view (a) and cross-sectional (b) scanning electron microscopy (SEM) images for the  $\text{CuGaSe}_2$  thin film grown on Mo/SLG substrate having a composition of  $[\text{Ga}]/[\text{Cu}] = 1.11$ , corresponding to a second growth time  $t_{g_2}$  of 7 min (table 3.1)

According to top-view SEM micrographs in the figure 3. 6 (a), the films possess triangular-like grain shapes having sizes of up to  $2 \mu\text{m}$ . This figure also exhibits the  $\langle 221 \rangle$  preferential growth direction with  $[\text{Ga}]/[\text{Cu}]$  ratios between 0.99 and 1.11. It was reported that such a morphology is typical of films grown from a Ga-rich phase [60]. Figure 3.6 (b) shows the cross-sectional scanning electron microscopy (SEM)- image for the films with composition of  $[\text{Ga}]/[\text{Cu}] = 1.11$  and indicates that the films are densely packed and, in some places, tend to grow in a columnar structure.

### 3.3 Concluding remarks

The novel chemical closed- space vapor transport (CCSVT) technique has been developed for the growth of single phase  $\text{CuGaSe}_2$  thin films. Cu precursors deposited on clean or Mo-coated soda lime glass (SLG) substrates are thermally and chemically treated under gaseous  $\text{GaCl}_x/\text{H}_2\text{Se}$  atmosphere in the CCSVT cell. The  $\text{Ga}_2\text{Se}_3$  employed as source material is stoichiometrically volatilized at  $550^\circ\text{C}$  by a controlled amount of  $\text{HCl}/\text{H}_2$  agent at a certain pressure.  $\text{CuGaSe}_2$  films are prepared with a growth rate of 230 - 240 nm/min by using a single stage process. A two stage process is applied for the fine tuning of the  $\text{CuGaSe}_2$  composition and electronic properties. Thin films of  $\text{CuGaSe}_2$  deposited by the CCSVT method onto soda lime glass (SLG) coated with a conducting Mo film or onto plain SLG were found to be polycrystalline with a strongly preferred (221) orientation. Single phase  $\text{CuGaSe}_2$  thin films grow in the compositional range of  $1.0 \leq [\text{Ga}]/[\text{Cu}] \leq 1.3$ , corresponding to a thickness range of  $1.6 \mu\text{m}$  to  $1.9 \mu\text{m}$ .