Chapter 6

Conclusions and Suggestions

In this thesis the growth of $CuIn_{1-x}Ga_xSe_2$ polycrystalline thin films with the wide range of Ga-content (x≡[Ga]/([In]+[Ga])) and Cu-content (y≡[Cu]/([In]+[Ga])), using molecular beam deposition technique have been investigated. The accomplishment of this work were concluded as the following.

(i) The characteristics of the MBE system including the calibration of substrate temperature, effusion cells were obtained and used to calculate the temperature profiles of $Cu(In,Ga)Se_2$ thin films growth process.

(ii) *In situ* monitoring technique was used to successfully control the final composition of films and detect the end of both two- and three-stage process.

(iii) The high quality $CuIn_{1-x}Ga_xSe_2$ films with a wide composition range of $0 \leq x \leq 1$ can be fabricated by MBD method using both two- and three-stage process,

(iv) The high quality $CuGaSe_2$ films and the difference between the growth mechanism of $CuGaSe_2$ grown by two-stage and three-stage were presented.

(v) And, the complete fabrication of $CuIn_{1-x}Ga_xSe_2$ thin film solar cells with high performances was successfully developed.

The most important results that followed from the respective studies summarized below:

- In order to investigate the influence of gallium in $CuInSe_2$ thin films, the $CuIn_{1-x}Ga_xSe_2$ with a composition range of $0 \leq x \leq 1$ films were prepared using the two-stage growth process with *in situ* monitoring technique. The *in situ* signals; T_{pyro} and OP were used to predict and detect the end point of the growth process. Typically, the final composition of films is $y \approx 0.9$. In this work, the shift in band gap with x was observed by transmission and reflection measurements. The optical parameters; refractive index, n, optical absorption coefficient, α, of each composition was also determined. The plot of the α versus x revealed that at $x = 1$ or $CuGaSe_2$ film, the free exciton absorption peak was clearly observed at room temperature, indicating high quality films.
- To investigate the evolution of morphology and structure of $CuGaSe_2$ films, the $CuGaSe_2$ films with wide range of y (Cu content) from 1.45 to 0.70 were fabricated using both two-stage and three-stage process. SEM and XRD investigation revealed that the morphological properties of these films were significantly influenced by the Cu content. In the case of two-stage growth process, XRD results indicated sharp well-defined chalcopyrite peaks with a strong preferred (112) orientation. The partial formation of $CuGaSe_2$ as well as the presence of the expected binary phases i.e. Cu_2Se (at the end of stage-1), Ga_2Se_3 (at the end of stage-2) was also observed. Moreover, no significant 2θ shift of the (112) peak was observed in the extended Cu-poor ($y \approx 0.7$) film. This result implied that the $CuGaSe_2$ film is stable chalcopyrite structure and can be tolerate an excess Ga_2Se_3 over Cu_2Se without precipitation of extra diffraction peaks caused by the ordering of vacancies in the defect-chalcopyrite structures. In the case of three-stage growth process, XRD results revealed that the $CuGaSe_2$ films show weakly (112) preferred orientation with chalcopyrite structure and no indication of any distortion. However, the SEM results indicated that the $CuGaSe_2$ films grown by three-stage have crevices (between

the $CuGaSe_2$ grain boundaries) less than that of the $CuGaSe_2$ films grown by two-stage process. Therefore, the three-stage process would be expected to fabricate the high quality $CuGaSe_2$ film with suitable properties for wide band gap absorber.

- The cell performances of the $CuIn_{1-x}Ga_xSe_2$ thin film solar cell revealed that the high device quality $CuIn_{1-x}Ga_xSe_2$ films with $x<0.7$ can be fabricated to give the high performance solar cells. We achieved the best cell (with an active area of 0.475 cm^2) with efficiency of 15.3% (without AR) using $CuIn_{1-x}Ga_xSe_2$ ($x=0.3$) grown by three-stage process as absorber layer.
- The $CuGaSe_2$-based solar cell with $CuGaSe_2$ grown by three-stage had improved V_{OC} values compared to the $CuGaSe_2$-based solar cell with $CuGaSe_2$ grown by two-stage. The V_{OC} values of $CuGaSe_2$ three-stage samples were around 750 mV, while the V_{OC} of $CuGaSe_2$ two-stage samples was around 650 mV. This result indicated that there are difference properties of films between the films grown by two-stage and three-stage process which consistent with the XRD and SEM studies.

As a result of the finding in this research, further suggestions for future studies could be the followings:

(1) For a better understanding of the influence of Ga content in the $CuInSe_2$ films, the $CuIn_{1-x}$ Ga_xSe_2 films should be characterized using high resolution XRD and TEM to obtain the re-orientation of the crystallite and the growth of the grains.

(2) For a understanding of the limitation of V_{OC} in the practical $CuGaSe_2$-based solar cell, the devices should be characterized by using the capacitance-voltage (C-V) and current-voltage measurements as a function of temperature to obtain the doping profiles and the energy band alignment of junction.