CHAPTER VI

CONCLUSIONS AND SUGGESTIONS

In this thesis the fabrication of $Cu(In,Ga)Se_2$ (CIGS) thin films for high efficiency solar cells have been investigated: (1) the development of the multi-source co-evaporation system with *in situ* monitoring for depositing high quality CIGS absorber layer, (2) the growth of CIGS films by two-stage or Cu-Rich-Off (CURO) process for high efficiency solar cells, (3) the growth of CIGS films by modified two-stage or Cu-Poor-Rich-Off (CUPRO) process for high efficiency solar cells. Conclusions based on the finding of the research were as follows:

(1) This research developed a high vacuum deposition system for the CIGS absorber layer at SPRL. This work is a prototype which includes design and construction of the system that focused on the four evaporation sources (Cu, In, Ga and Se) and the *in situ* monitoring signals (T_{pyro}, T_{sub} and OP). These sources were used to deposit the uniform CIGS film onto the substrate (area 5x6 cm^2). All *in situ* monitoring signals used in the growth process show the same End Point Detection (EPD) for the desired ratio of Cu-deficient content ($y \approx 0.9$) of CIGS film which was also confirmed by EDS. These signals were used as the control process and especially the point corresponding to the ratio of Cu content ($y \approx 0.9$) was established to be the end point for the growth process.

(2) At SPRL, the growth of CIGS thin films for high efficiency solar cells used a two-stage or CURO process. The CURO (or Cu-rich/Cu-off)

process modified from the bi-layer method developed by Boeing research group and added the end point detection (T_{pyro}, T_{sub} and OP). Using our CURO recipe, the CIGS films were found to be typically (112) oriented chalcopyrite, large columnar grains, rough surface with deep crevices between the CIGS grain boundaries at the top fraction of the film. The deep crevices are proposed as a good evidence that arises from the conversion of Cu_xSe to $Cu(In,Ga)Se_2$. These crevices can be as deep as the total film thickness. The two-stage growth model was proposed based on the analysis of our experimental results and the film formation mechanism was explained. Using the *in situ* monitoring technique, the high quality CIGS films were fabricated to give the high performance solar cells up to 14% (without anti-reflection (AR) coating).

(3) At ÅSC, the growth of CIGS thin films for high efficiency solar cells used a modified two-stage or CUPRO process. The CUPRO (or Cu-poor/Cu-rich/Cu-off) process has superior qualities for practical producibility. In order to obtain the simple end point detection method, the constant substrate temperature was used in the fabrication process. It also used the moderate temperature profiles between those of two-stage and three-stage processes. This CUPRO process varied only Cu-flux resulting in uniform CIGS films for high quality devices. The control of the process was considered into three steps; low Cu flux, high Cu flux, no Cu flux, whereas the five-stage growth model is proposed for the film formation mechanism. The first stage is the growth of a Cu-poor oriented weakly on (220)(204) plane with small grain layer. The second stage is recrystallization by Cu-diffusion until the composition of the film be stoichiometry. The third stage is overgrowth of the bi-phase system

$Cu(In,Ga)Se_2 + Cu_xSe$. The fourth stage is a consumption of the secondary Cu_xSe phase, and the fifth stage is attainment of the Cu-poor composition for device relevance (i.e. $y \approx 0.90$). The $Cu(In,Ga)Se_2$ layers resulting from this process was found to be oriented weakly on (220)(204) chalcopyrite plane and to have crevices of the depths determined by the layer thickness grown in the third stage. It is also hypothesized that these crevices result from the conversion of the Cu_xSe into $Cu(In,Ga)Se_2$ in the fourth stage of the growth, but they do not prevent the layers from being device quality, at about 15% (without AR coating) for less than 20 minute growths.

(4) The effect of substrate temperatures was also studied between 475 and 550°C. SEM and XRD measurements show these CIGS films to be large grain and dense, with increasing (220)(204) orientation as lower substrate temperatures were used. The higher substrate temperatures gave the CIGS films with lower Ga contents about 10% which confirmed by the clear shift of approximately 50 nm in the QE cut-off values as well as a J_{sc} versus V_{oc} trade-off in the I-V characteristics. However, the values of efficiency show more or less the same efficiency of 15%.

(5) The growth of CIGS films using CURO process (at SPRL) achieved the best efficiency of 14.2% which lowered than that of 15.9% of the films using CUPRO process (at ÅSC). These results show that these CIGS films fabricated from two processes have different qualities and also included the different base-line qualities for the device fabrications from two research centers.

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

(1) The CIGS deposition system for large area using an in-line process for moving substrate should be developed, where the control process via non-contact method should be considered.

(2) To better understand the recrystallization by Cu-diffusion in the CUPRO process, the intermediate stages of the films during the growth process should be characterized using high resolution TEM to obtain the re-orientation of the crystallite and the growth of the grains.