CHAPTER 4

EXPERIMENTAL PROCEDURE

This chapter concerns with the experimental procedure which involves a brief description of the fabrication techniques for each layer of the device, i.e. the stacking of Mo, CIGS, CdS and ZnO films on top of a glass substrate to form a Mo/CIGS/CdS/ZnO heterojunction thin film solar cells. However, the main goal of this research is to study the effect of the CdS layer deposited on CIGS film by Chemical Bath Deposition (CBD) technique with different deposition conditions as well as to study the junction characteristics by analyzing their current-voltage response.

4.1 Fabrication of Mo/Cu(In,Ga)Se$_2$/CdS/ZnO Thin Film Solar Cells

The structure of high efficiency polycrystalline Cu(In,Ga)Se$_2$-based thin film solar cell is shown in Fig. 4.1, 5 cm x 6 cm soda lime glass (SLG) is used as substrates for thin film solar cells. The back contact of the device is a 0.5 μm thick of Mo film coated on the soda lime glass by dc-magnetron sputtering. The Cu(In,Ga)Se$_2$ absorber layer was deposited on top of the Mo film by physical vapor deposition (PVD) method from four Knudsen-type sources. The four evaporation sources were independently controlled by PID temperature controllers to emit appropriate fluxes of Cu, In, Ga, and Se. The final CIGS layer with a nominal thickness of 2 μm and a composition of slightly Cu poor, [Cu]<[(In)+(Ga)], was

achieved by the modified bi-layer process. In this process, the temperature of the substrate was raised to a temperature very close to the softening temperature of the glass substrate (approximately 550 °C) and the temperatures of the four sources (Cu, In, Ga, and Se) were kept constant for a certain time T1. This first layer of the film was highly Cu-rich. In order to obtain the film with total composition of slightly Cu poor, the second layer was successively deposited without Cu by simply turning off the Cu source for a certain time (T2 – T1), where T2 is the total deposition time. By properly adjusting temperatures of Cu, In and Ga sources as well as the time T1 and T2, a slightly Cu poor $Cu(In,Ga)Se_2$ films with $[Ga]/[(In)+(Ga)] \approx 0.25$ corresponding to a bandgap (Eg) of ~ 1.15 eV can be obtained.
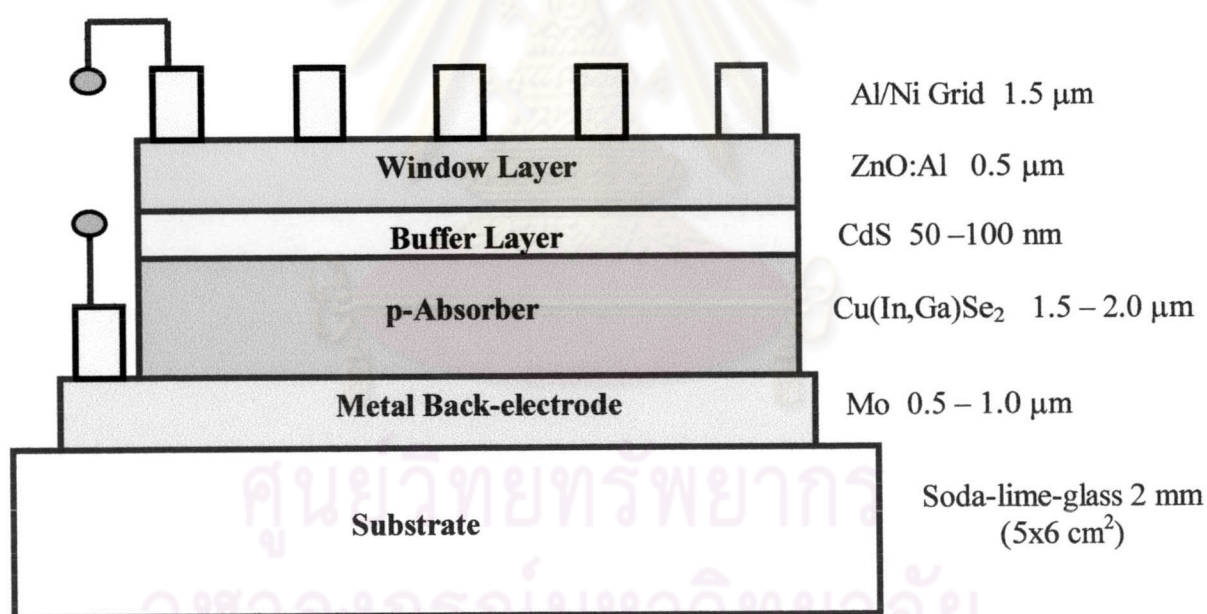

Figure 4.1: Schematic showing structure of polycrystalline CIGS-based thin film solar cells (not to scale).

For a conventional semiconductor material to be fabricated as a device such as a solar cell, the material must be characterized for its suitability for the device. In this case, however, there is no standard method to be used to check for the quality

of the films. The CIGS thin film must be converted to a complete solar cell and tested for its photovoltaic conversion efficiency. To complete the device structure, two more layers; the CdS buffer layer and a transparent conducting oxide (TCO) layer, are needed to form a heterojunction thin film solar cell. The CdS buffer layer with thickness of ~ 50-80 nm was deposited by CBD technique. The TCO film front layer is ZnO which is deposited by RF-magnetron sputtering from a target made from ZnO + 2 wt % Al_2O_3. The TCO over layer was actually a bi-layer film. The first layer on top of the CdS film is a highly resistive (50 nm thick) layer deposited by reactive sputtering   (Ar + 4 at. % O_2) from the same ZnO target. The 500 nm top layer of the TCO film is a highly conductive layer deposited by using pure Ar gas. The front metallic grids are fork-shape Ni/Al film deposited by thermal evaporation through a metallic mask. Each metallic grid is designed to give an individual cells with area ~0.48 cm^2 with an ~2.5% shading loss. This is shown in Fig. 4.2. After completion of the device, the whole piece was scribed into ~ 45 cells of total area of ~ 0.48 cm^2. Electrical and photovoltaic conversion response of each cell was studied by current-voltage (J-V) measurement at 25 °C under AM1.5 illumination. Light soaking effect and temperature dependence of the J-V characteristics were investigated on some selected cells.
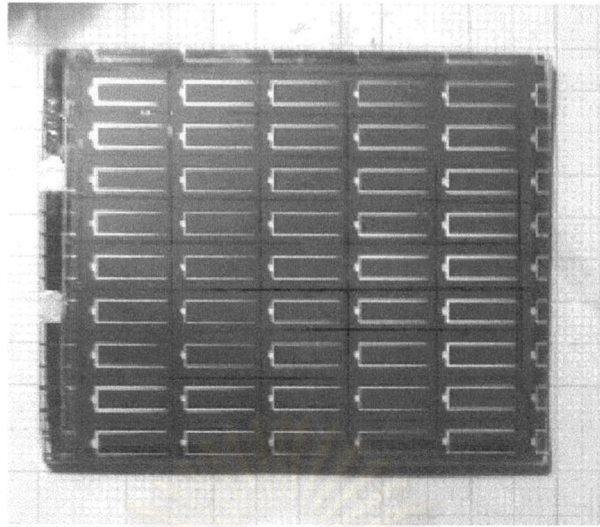
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Figure 4.2: Photograph of Mo/Cu(In,Ga)Se$_2$/CdS/ZnO heterojunction thin film solar cells fabricated at the Semiconductor Physics Research Laboratory. There are 40 individual cells on the sample area of 5x6 cm^2.
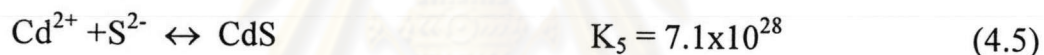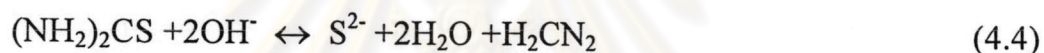
4.2 Chemical Bath Deposition of CdS Layer[16, 17]

For the fabrication of a high efficiency Cu(In,Ga)Se$_2$ [CIGS] based solar cell, thin layer of cadmium sulfide (CdS) is deposited prior to ZnO. The CdS plays an essential role in the creation of semiconductor junction on the surface of the p-type CIGS absorber layer. CdS films can be grown by several methods such as thermal evaporation under high vacuum. However, CdS thin film on top of the CIGS layer is normally deposited by the CBD method for high efficiency CIGS based thin film solar cells. Not only does this technique enable total coverage for very thin layer (10-50 nm) on rough polycrystalline surface of the CIGS layer but it is also a low temperature (≈ 60 °C) process. When the CBD technique is used, the bath chemicals may interact with the CIGS surface and possibly modify it. Therefore, the CBD is not only a deposition step but also a surface modification for the CIGS film.

However, the optimized parameters for the absorber prior to standard sputtering window layers may not be the same.

4.2.1 The Growth Kinetics of CBD-CdS [18]

The CBD process for this experiment involved the reaction of thiourea with cadmium sulfate ($CdSO_4$) in ammonia-buffered aqueous solution at 60 °C. The various reactions involved and their equilibrium constants at room temperature are as follows

$$NH_3 + H_2O \leftrightarrow NH^+_4 + OH^- \qquad K_1 = 1.8 \times 10^{-5} \qquad (4.1)$$

$$Cd^{2+} + 2OH^- \leftrightarrow Cd(OH)_2 \qquad K_2 = 1.88 \times 10^{14} \qquad (4.2)$$

$$Cd^{2+} + 4NH_3 \leftrightarrow Cd(NH_3)_4^{2+} \qquad K_3 = 3.6 \times 10^6 \qquad (4.3)$$

$$(NH_2)_2CS + 2OH^- \leftrightarrow S^{2-} + 2H_2O + H_2CN_2 \qquad (4.4)$$

$$Cd^{2+} + S^{2-} \leftrightarrow CdS \qquad K_5 = 7.1 \times 10^{28} \qquad (4.5)$$

Although the above chemical reactions look straight forward. However, purity and forms of chemicals involved, especially the thiourea, play an important role in the CBD process. In order to obtain high quality CdS film on CIGS, physical appearance as well as electrical characteristics, optimum deposition conditions has to be determined.

4.2.2 Preparation of the CBD-CdS Buffer Layers [18]

For routine deposition of CdS films by CBD method, stock solution of specific concentration of $CdSO_4$, $(NH_2)_2CS$ and NH_3-solution were prepared in advance. In this work, however, three different concentrations of $(NH_2)_2CS$ solution were used. The idea of using difference concentrations of $(NH_2)_2CS$ is to study the effect of impurities in the CdS films which are derived from the bath solution. The

deposition process was carried out by mixing appropriate proportions of $CdSO_4$, $(NH_2)_2CS$ and NH_3-solution as shown in Table 4.1.

Table 4.1: Growth conditions of CBD-CdS buffer layers

	type 1	type 2	type 3
Concentration Ratio (M) ($CdSO_4 : NH_3 : SC(NH_2)_2$)	0.004 : 4.0 : 0.06	0.004 : 4.0: 0.03	0.004 : 4.0 : 0.1
Volume Ratio (cm^3) ($CdSO_4 : NH_3 : SC(NH_2)_2$)	40 : 40 : 80	40 : 40 : 80	40 : 40 : 80
Chemical Bath Temperature (°C)	60	60	60
Deposition Time (minutes)	8	10	6

In addition, the pH of the chemical bath solution was kept in the range of 10.5 - 11.5 by adjusting the NH_3-solution. Figure 4.3 shows the schematic of the CBD apparatus. The sample to be coated by CdS (soda-lime-glass(SLG)/Mo/ $Cu(In,Ga)Se_2$) was then immersed in the chemical bath solution and the beaker was immediately placed in the water bath which was kept at 60 °C. During the deposition process, the solution was stirred by magnetic stirrer. The thickness of CBD-CdS layer was estimated to be 50-80 nm depending on the deposition time (typically 600 seconds). Immediately after the deposition, the sample was rinsed in de-ionized (DI) water and blown dry with nitrogen gas. Pictures of chemical bath solutions, CBD set-up during deposition of SLG/Mo/$Cu(In,Ga)Se_2$ sample and the sample after the deposition process are shown in Figs 4.4 – 4.5.
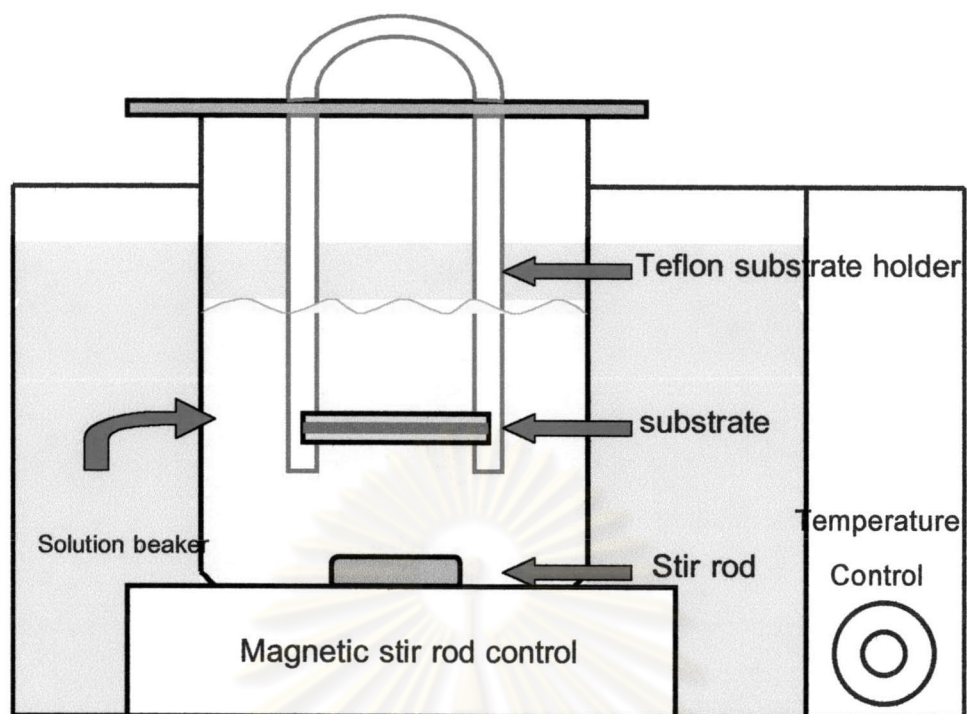
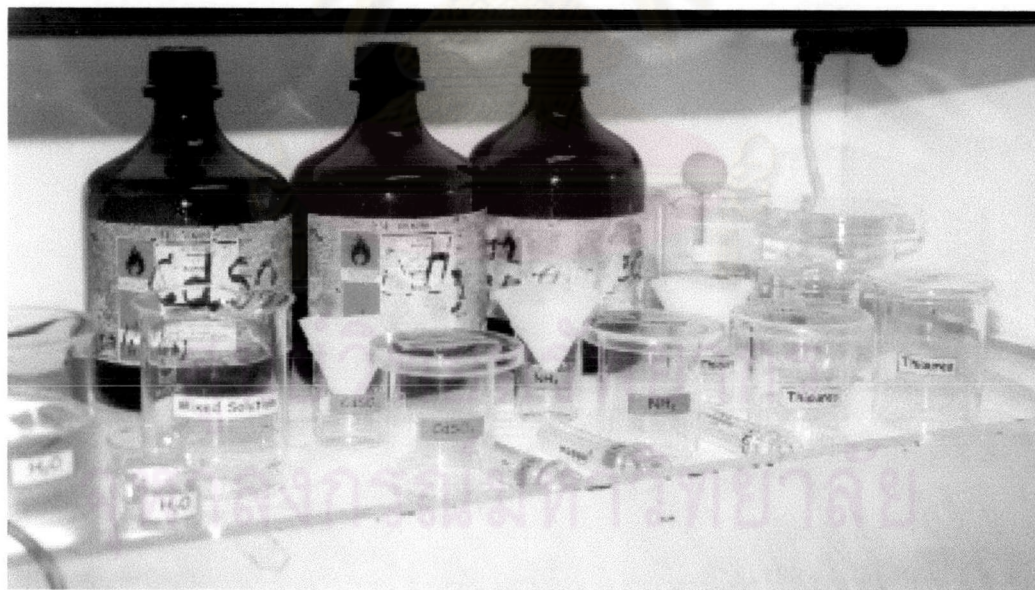**Figure 4.3:** Schematic of chemical bath deposition technique (not to scale).

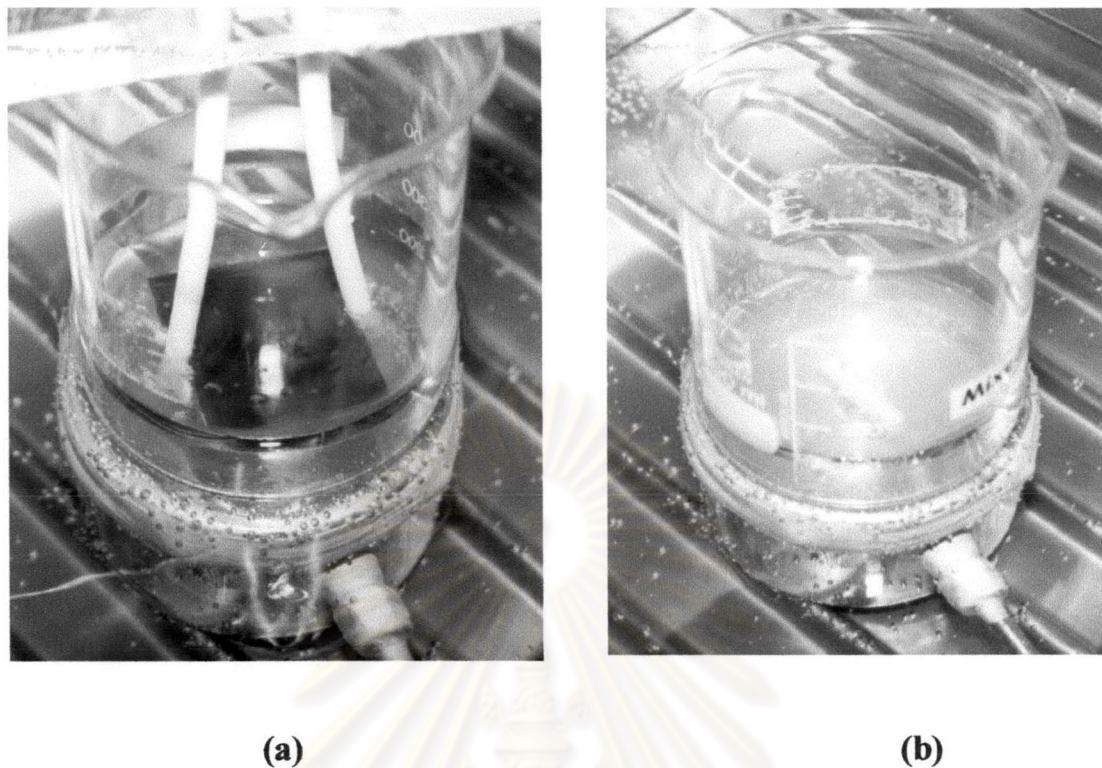**Figure 4.4:** Photograph of the chemical solutions used in the chemical bath deposition.

(a) **(b)**

Figure 4.5: Photograph of the chemical bath deposition; (a) The SLG/Mo/Cu (In,Ga)Se$_2$ sample during the deposition. (b) After the sample was removed from the chemical bath solution.

4.3 Standard Current-Voltage (J-V) Measurement

The standard J-V measurements of the solar cells were made in the dark and under the ELH type halogen lamp illumination (used to simulate an AM1.5 solar spectrum, normalized to 100 mW/cm^2) at 25±2 °C (see in Fig. 4.6). Keithley source-measurement unit model 238 was used as current source and voltage measurement. IEEE-488 interface card and a PC enable the system to be fully computerized. From such measurements the open-circuit voltage V_{oc}, the short-

circuit current I_{sc} and the fill factor FF can be readily obtained. The photograph

and diagram of the J-V measurement system are shown in Figs. 4.6 – 4.8.

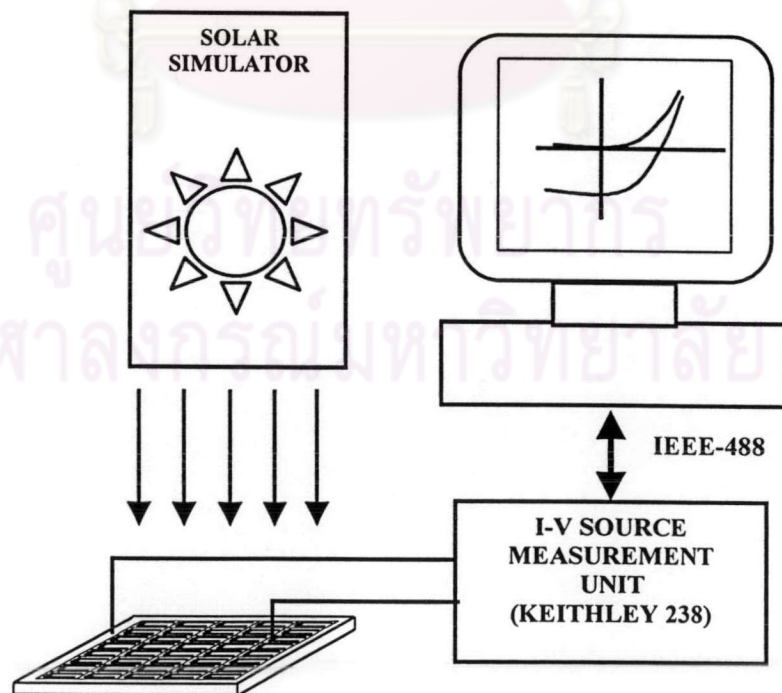**Figure 4.6:** Photograph of the J-V measurement system.

Figure 4.7: Schematic (not to scale) of J-V measurement system.
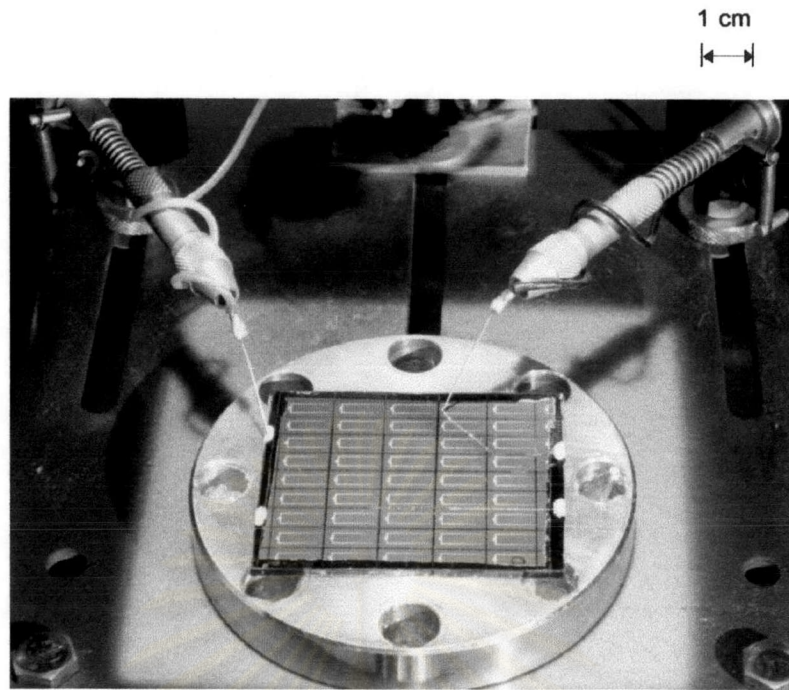
Figure 4.8: Photograph of J-V measurement during illumination.

4.3.1 Analysis of the J-V Characteristic

The analysis of the room temperature J-V characteristic was carried out to characterize the diode behavior. When an external voltage is applied across a device, a net current can flow through the junction. The J-V data under illumination can be represented in terms of a forward diode current and light generated current in opposite direction, is expressed by the equation [19, 20]

$$J = J_0 \left[\exp\left(\frac{q(V - R_s J)}{AkT} \right) - 1 \right] - J_L + GV , \qquad (4.6)$$

where J_0 is the forward current, J_L is the light generated current, A is the diode ideality factor, R_s is the series resistance, G is the shunt conductance, k is the Boltzmann constant, and T is the absolute temperature.

With the forward diode current limited by Shockley-Red-Hall recombination through a distribution of states within the space charge region of the absorber layer, A takes a value between 1 and 2.

The forward current J_0 can be expressed by the equation

$$J_0 = J_{00} \exp\left[-\frac{E_g}{2kT}\right],$$ (4.7)

where J_{00} is a constant.

For simplicity, R_s and G are assumed to take constant values, i.e. the series and shunt terms are ohmic. J_L can be voltage dependent, but most diode analysis requires the assumption that the light generated current is constant, i.e. $J_L = J_{sc}$. The value of G can be obtained from the minimum value of the slope dJ/dV in the reverse bias configuration. From the value of G, $J' = J - GV$ can be obtained. From the assumption that R_s and J_{sc} are constant, we can differentiate Eq. (4.6) to give

$$\frac{dV}{dJ'} = R_s + \frac{AkT}{q}(J' + J_{sc})^{-1}.$$ (4.8)

In this case, a plot of dV/dJ' versus $(J + J_{sc})^{-1}$ is linear at large current with intercept R_s and slope AkT/q. Finally, when the assumptions of constant R_s, G, and J_L are applied and Eq. (4.6) is shown to be applicable, a logarithmic plot of $J' + J_{sc}$ versus $V - R_sJ'$ gives an intercept of J_0 and slope q/AkT.

Solving Eq. (4.6) for $J = 0$, with $GV_{oc} \ll J_{sc}$, gives

$$qV_{oc} = \frac{A}{2}E_g + AkT\ln\left(\frac{J_{sc}}{J_{00}}\right).$$ (4.9)

4.3.2 Current - Voltage Dependent of Temperature - J(V,T) Measurement

For temperature dependent J-V measurement, the samples (Cu(In,Ga)Se$_2$-based thin film solar cell) were mounted on the available vertical platform stage in a vacuum chamber. The system was designed with the capability to cool down by a set of movable cold finger in the liquid nitrogen reservoir and to heat up to the desired temperature in range 130K – 480K. The programmable temperature controllers were used during heat up process. The programmable J-V measurement unit as described previously was also use for this measurement. The ELH type halogen lamp was used to simulate an AM1.5 solar spectrum. Measurement procedure was started at 150K with the dark J-V curves followed by measurements under illumination before increasing the temperature.
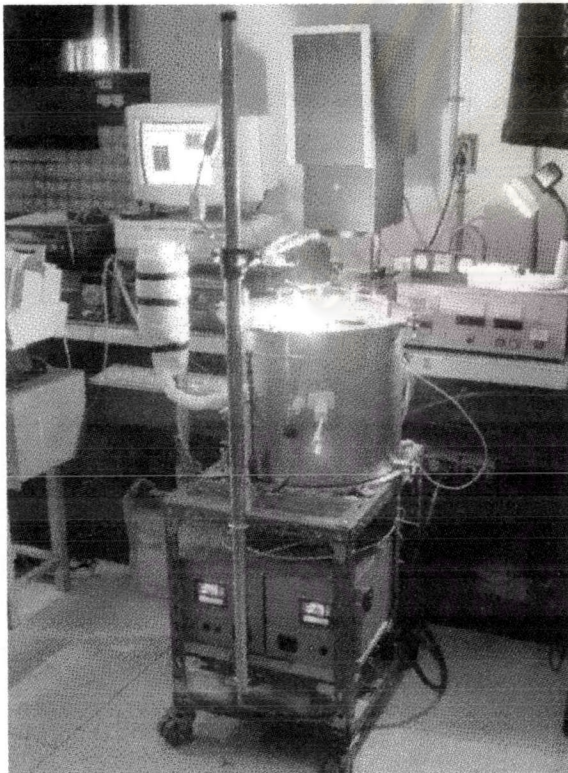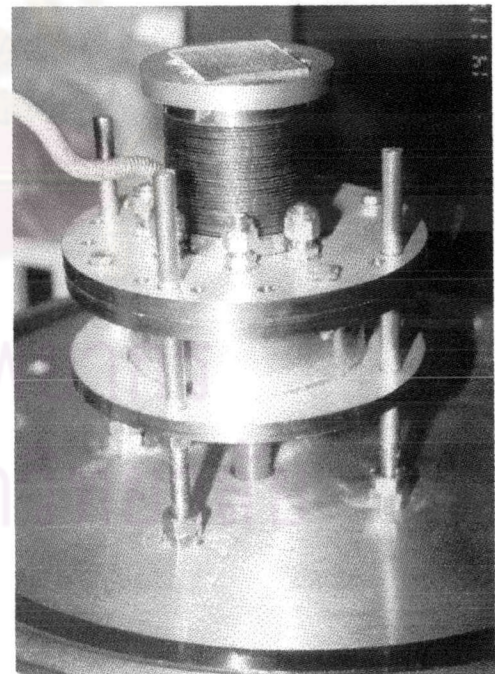
(a)   (b)

Figure 4.9: (a) Photograph of the J(V,T) measurement system. **(b)** The sample on the movable cold finger in the liquid nitrogen reservoir.

4.4 Conclusions

In this chapter, I have briefly described of the fabrication methods for each layer of the Cu(In,Ga)Se$_2$-based thin film solar cell, with emphasis on the CdS buffer layer. I also described the J-V measurement-system setup, including the physical model used to characterize the J-V characteristic of Cu(In,Ga)Se$_2$-based thin film solar cells.