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Appendices

Appendix A

List of Symbols and Abbreviations

Symbols

a	Lattice constant
a-Si	Amorphous silicon
A	Diode ideality factor
α	Absorption coefficient
b	Bowing parameter
c	Lattice constant
d	Lattice plane spacing
Δ_{cf}	Crystal-field splitting
Δm	Molecularity deviation
Δs	Stoichiometry deviation
Δ_{so}	Spin-orbit splitting
D_e, D_h	Diffusion coefficient of electron, hole
ε	Emissivity
E_c	Conduction band energy
E_v	Valence band energy
E_F	Equilibrium Fermi level
FF	Fill Factor
E_g	Band gap energy
Γ	Flux

In_{Cu}	Indium on copper anti-site defect
I, I_{SC}	Current, short circuit current
I_L	Light-generated current
I_M	Maximum current (of solar cells)
I_0	Diode saturation current
I(z)	Ionization coefficient
J, J_{SC}	Current density, short circuit current density
J_0	Saturation current density
k	Boltzmann constant
L_e, L_h	Diffusion length of electron, hole
M	Molecular weight
n	Free electron density
n_i	Intrinsic carrier concentration
N	Avogadro's number
N_A, N_D	Effective density of state for electron, hole
N_C	Effective density of states in the conduction band
N_V	effective density of states in the valence band
p	Free hole density
p_{BA}	Pressure reading from pressure gauge
P_{in}	Incident power
P_M	Maximum power output (of solar cells)
q	Electrical charge
r	Deposition rate
R	Reflectance, Reflectivity, Gas constant
R_S	Series resistance
R_{SH}	Shunt resistance
ρ	Density

T	Transmittance, Transmissivity, Absolute temperature
T_m	Melting point temperature
T_{sub}	Substrate temperature
T_{pyro}	Substrate temperature reading by pyrometer
θ	X-ray diffraction angle
v_{th}	Thermal velocity
V_{Cu}	Copper vacancy defect
V_{OC}	Open-circuit voltage
V_M	Maximum voltage (of solar cells)
x	[Ga]/([In]+[Ga]) atomic ratio
y	[Cu]/([In]+[Ga]) atomic ratio
z	Atomic number
z_{rms}	Root-mean-square roughness

Abbreviations

AM1.5	Standard terrestrial solar spectrum "Air Mass 1.5"
AFM	Atomic force microscopy
AR	Anti-reflection
BEP	Beam equivalent pressure
BFM	Beam flux monitor
CBD	Chemical bath deposition
CGS	Copper gallium diselenide ($CuGaSe_2$)
CIS	Copper indium diselenide ($CuInSe_2$)
CIGS	Copper indium gallium diselenide ($CuIn_{1-x}Ga_xSe_2$)
DC	Direct current (for sputtering process)
DI	de-ionized water
EDX	Energy-dispersive X-ray spectroscopy
EPD	End-point detection
FE	Free exciton
FWHM	Full width at half maximum
I-V	Current versus voltage [curve]
JCPDS	Joint committee on powder diffraction standards
J-V	Current density versus voltage [curve]
K-cell	Knudsen cell, effusion cell
MBD	Molecular beam deposition
MBE	Molecular beam epitaxy
NDC	Neutral defect complex
NREL	National renewable laboratory
ODC	Ordered defect chalcopyrite
OP	Output power of temperature controller

OVC	Ordered vacancy compound
PBN	Pyrolytic boron nitride
PID	Proportional integral derivative
PV	Photovoltaic
PVD	Physical vapor deposition
QMS	Quardrupole mass spectroscopy
QCM	Quartz crystal thickness monitor
RF	Radio frequency (for sputtering process)
RGA	Residual gas analyzer
RHEED	Reflection high energy electron diffraction
SEM	Scanning electron microscopy
TC	Substrate temperature (thermocouple reading)
TCE	Trichloroethylene
TCO	Transparent conducting oxide
TSP	Titanium sublimation pump
XRD	X-ray diffraction
UHV	Ultra high vacuum

Appendix B

General Calculation for $CuIn_{1-x}Ga_xSe_2$ Deposition Process

For $CuIn_{1-x}Ga_xSe_2$ films, the chemical composition is commonly defined by the atomic ratios y = [Cu]/([In]+[Ga]) and x = [Ga]/([In]+[Ga]). The [Cu]/([In]+[Ga]) ratio largely affects the film morphology while the [Ga]/([In]+[Ga]) ratio determines the band gap of the absorber layer. These parameters (x and y) are also used to characterize the composition of $Cu(In,Ga)Se_2$ material. During the growth process, these parameters as a function of time can be expressed as:

$$y = \frac{N_{Cu}}{N_{In} + N_{Ga}}, \tag{B.1}$$

and

$$x = \frac{N_{Ga}}{N_{In} + N_{Ga}}. \tag{B.2}$$

Here N_i is the number of atoms of specie i accumulated in the growing film at time t.

Consider both y and x in a unit area of $Cu(In,Ga)Se_2$ film with a total thickness of d_{CIGS}. From Eqs. (B.1) and (B.2) the more general form of the atomic ratios can be written as:

$$y = \frac{d_{Cu} \cdot \rho_{Cu} \cdot M_{Cu}^{-1} \cdot A \cdot N_A}{(d_{In} \cdot \rho_{In} \cdot M_{In}^{-1} + d_{Ga} \cdot \rho_{Ga} \cdot M_{Ga}^{-1}) \cdot A \cdot N_A}, \tag{B.3}$$

and

$$x = \frac{d_{Ga} \cdot \rho_{Ga} \cdot M_{Ga}^{-1} \cdot A \cdot N_A}{(d_{In} \cdot \rho_{In} \cdot M_{In}^{-1} + d_{Ga} \cdot \rho_{Ga} \cdot M_{Ga}^{-1}) \cdot A \cdot N_A}, \tag{B.4}$$

where d_i is the film thickness of metal i at time t ,

ρ_i is the density of the metal i,

M_i is the mass per mole of the metal i, A is the unit area of the growing film,

and N_A is Avogadro's constant.

The numerical values of the parameters are given in Table B.1.

Table B.1: Density and mass per mole values of the materials.

Material	ρ (g/cm^3)	M (g/mole)
Cu	8.96	63.55
In	7.31	114.82
Ga	5.91	69.72
Se	4.79	78.96
$CuInSe_2$	5.89	336.29
$CuGaSe_2$	5.27	291.19

To simplify the expressions of y and x in Eqs. (B.3) and (B.4) respectively, we will define the parameter α_i as the following:

$$\alpha_{Cu} = \rho_{Cu} \cdot M_{Cu}^{-1}, \quad \text{(B.5a)}$$

$$\alpha_{In} = \rho_{In} \cdot M_{In}^{-1}, \quad \text{(B.5b)}$$

and

$$\alpha_{Ga} = \rho_{Ga} \cdot M_{Ga}^{-1}, \quad \text{(B.5c)}$$

where the numerical values are given in Table B.2.

Table B.2: α parameter of the elements.

Material	α ≡ ρ/M (mole/cm^3)
Cu	0.1410
In	0.0637
Ga	0.0848
Se	0.0607

Substitute Eqs (B.5a), (B.5b) and (B.5c) back into Eqs. (B.3) and (B.4), we will get the relations of the corresponding metal film thicknesses,

$$d_{In} \cdot \alpha_{In} + d_{Ga} \cdot \alpha_{Ga} = d_{Cu} \cdot \alpha_{Cu} \cdot \frac{1}{y} = d_{Ga} \cdot \alpha_{Ga} \cdot \frac{1}{x}. \quad \text{(B.6)}$$

Rearrange Eq. (B.6), we obtain

$$d_{Ga} = \frac{x}{y} \cdot \frac{\alpha_{Cu}}{\alpha_{Ga}} \cdot d_{Cu}, \quad \text{(B.7a)}$$

and

$$d_{In} = \frac{(1-x)}{y} \cdot \frac{\alpha_{Cu}}{\alpha_{In}} \cdot d_{Cu}. \quad \text{(B.7b)}$$

According to the fact that at constant source temperature, the thickness d_i is proportional to the deposition rate of element i; r_i, and the deposition time t_i. Thus

$$d_i = r_i \cdot t_i, \quad \text{(B.8)}$$

Then, Eqs (B.7a) and (B.7b) can be rewritten as

$$r_{Ga} = \frac{x}{y} \cdot \frac{\alpha_{Cu}}{\alpha_{Ga}} \cdot r_{Cu}, \quad \text{(B.9a)}$$

and

$$r_{In} = \frac{(1-x)}{y} \cdot \frac{\alpha_{Cu}}{\alpha_{In}} \cdot r_{Cu}. \quad \text{(B.9b)}$$

Eqs. (B.7a) and (B.7b) show the relation between the thickness of In and Ga films and the final composition and the thickness of Cu film. For example: stoichiometric $CuInSe_2$ i.e. x=0, y=1, we obtain $d_{In} = 2.214\, d_{Cu}$, and for stoichiometric $CuGaSe_2$ i.e. x=1, y=1, we obtain $d_{Ga} = 1.663\, d_{Cu}$.

The relation between the thickness of the $Cu(In,Ga)Se_2$ layer and the thickness of the corresponding Cu film made from the Cu contents of the $Cu(In,Ga)Se_2$ can be calculated as

$$\frac{d_{Cu}}{d_{CIGS}} = \frac{V_{Cu}}{V_{CIGS}} = \frac{N_{Cu} \cdot M_{Cu} / \rho_{Cu}}{N_{CIGS} \cdot M_{CIGS} / \rho_{CIGS}}, \quad \text{(B.10)}$$

where V_{Cu} is the volume of copper layer,

V_{CIGS} is the volume of $Cu(In,Ga)Se_2$ layer,

N_{Cu} is the number of copper atoms in the volume V_{Cu},

and N_{CIGS} is the number of $Cu(In,Ga)Se_2$ molecules in the volume V_{CIGS}.

Due to the fact that $Cu(In_{1-x}Ga_x)Se_2$ layer is an alloy of two compounds, $CuInSe_2$ (x=0) and $CuGaSe_2$ (x=1). Hence, M and ρ are functions of x, then Eq. (B.10) can be written as

$$\frac{d_{Cu}}{d_{CIGS}} = \frac{N_{Cu} \cdot (M_{Cu}) \cdot (\rho_{CIS} \cdot (1-x) + \rho_{CGS} \cdot x)}{N_{CIGS} \cdot (M_{Cu} + M_{In} \cdot (1-x) + M_{Ga} \cdot x + 2 \cdot M_{Se}) \cdot (\rho_{Cu})}. \qquad (B.11)$$

The ratio of N_{Cu} and N_{CIGS} is equal to unity. For example: $CuInSe_2$, we obtain: $d_{Cu} = 0.124\, d_{CIGS}$, and for $CuGaSe_2$, we obtain: $d_{Cu} = 0.128\, d_{CIGS}$.

Appendix C

List of Publications:

1. Chityuttakan, C., Chinvetkitvanich, P., Yoodee, K., and Chatraphorn, S. *In situ* Monitoring of the Growth of Cu(In,Ga)Se_2 Thin Films. *Sol. Energy Mater. Sol. Cells*. **90** (2006): 3124-3129.

2. Chinvetkitvanich, P., Chityuttakan, C., Yoodee, K., and Chatraphorn, S. Growth and Characterization of Cu-Ga-Se Thin Films Grown by Molecular Beam Deposition Method. *The 15th International Photovoltaic Science and Engineering Conference (PVSEC15)*: 2005, Shanghai, China: 602-603.

3. Chityuttakan, C., Chinvetkitvanich, P., Yoodee, K., and Chatraphorn, S. Optical Absorption Characteristics of Cu-Ga-Se Thin Films Grown by Molecular Beam Deposition Method, *The 15th International Photovoltaic Science and Engineering Conference (PVSEC15)*: 2005, Shanghai, China: 1158-1159.

4. Chinvetkitvanich, P., Chityuttakan, C., Chatraphorn, S., Chatraphorn, S., and Yoodee, K. Structural Evolution and Optical Characterization of Cu-Ga-Se Thin Films Grown by Molecular Beam Deposition Method. (submitted for publication in Thin Solid Films 2006)

5. Chinvetkitvanich, P., Chityuttakan, C., Yoodee, K., and Chatraphorn, S. Growth and Characterization of Cu-Ga-Se Thin Films Grown by Molecular Beam Deposition Method. (accepted for publication in Solar Energy Materials & Solar Cells)

Publications related to this work:

1. Arthibenyakul, B., Chinvetkitvanich, P., Chityuttakan, C., Chatraphorn, S., Yoodee, K., and Chatraphorn, S. Surface Properties of Molecular Beam Epitaxy Grown Copper-Indium_diselenide on Gallium-Asenide Substrate Observed by Reflection High Energy Electron Diffraction. *Proceedings of 31th Congress on Science and Technology of Thailand*: 2005, 191.

2. Chityuttakan, C., Chinvetkitvanich, P., Yoodee, K., and Chatraphorn, S. *In situ* Monitoring Signals of the Fabrication of $Cu(In,Ga)Se_2$ Thin Films for High Efficiency Solar Cells. *Proceedings of 31th Congress on Science and Technology of Thailand*: 2005, 242.

3. Preechaburana, P., Chityuttakan, C., Chinvetkitvanich, P., Yoodee, K., and Chatraphorn, S. Fabrication of $Cu(In,Ga)Se_2$-based Thin Film Solar Mini-modules module. *Proceedings of 31th Congress on Science and Technology of Thailand*: 2005, 313.

4. Chinvetkitvanich, P., Chityuttakan, C., Chatraphorn, S., Yoodee, K., and Chatraphorn, S. Analysis of High Quality $CuGaSe_2$ Thin Films Grown by Molecular Beam Deposition Method. *Proceedings of 4th Thailand Materials Science and Technology Conference*: 2006, 82.

5. Chityuttakan, C., Chinvetkitvanich, P., Chatraphorn, S., and Chatraphorn, S. Influence of Deposition Parameters on the Quality of ITO Films for Photovoltaic Application. Proceedings *Proceedings of 4th Thailand Materials Science and Technology Conference*: 2006, 94.

Awards:

1. PVSEC Award for best oral presentation:

    Chinvetkitvanich, P., Chityuttakan, C., Yoodee, K., and Chatraphorn, S. Growth and Characterization of Cu-Ga-Se Thin Films Grown by Molecular Beam Deposition Method. *The 15th International Photovoltaic Science and Engineering Conference (PVSEC15)*: 2005, Shanghai, China.

2. Ms@t Award (for best student paper award in ceramics session):

    Chinvetkitvanich, P., Chityuttakan, C., Chatraphorn, S., Yoodee, K., and Chatraphorn, S. Analysis of High Quality $CuGaSe_2$ Thin Films Grown by Molecular Beam Deposition Method. *The 4th Thailand Materials Science and Technology Conference*: 2006, Phatumthani, Thailand.

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