Keynote Address
4th Int. Seminar on Green Energy Conversion

山梨大学
UNIVERSITY OF YAMANASHI

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YEAR OF LIGHT
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Compound Semiconductor-based Solar Cells

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Self Introduction

- 1968-1984 Research on ternary magnetic semiconductors at Broadcasting Science Research Lab of NHK
- 1984-2007 Basic and application research of ternary compound semiconductors such as $CuInSe_2$, $CuGaSe_2$, as well as chalcopyrite type magnetic semiconductors $CdGeP_2$:Mn
- 1994 Installation of 3kW-PV system in my house still working now.
- 2011 Publication of a book “Fundamentals of Solar Cells”

Outline of this Lecture

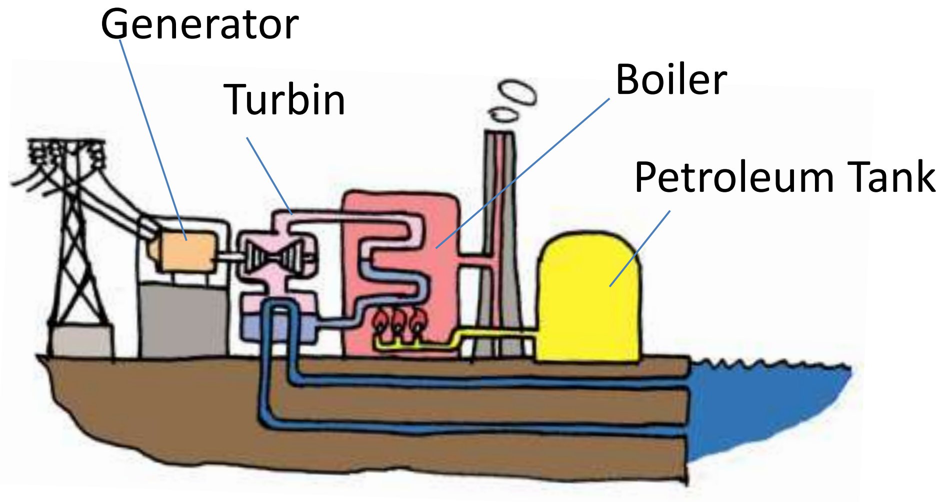
- Why solar cells now?
- How much is the power of the sunshine per $1m^2$?
- Can you tell the visible wavelength range of light?
- Why can we get electricity from solar irradiation?
- What device is necessary to convert the light to electricity?
- How much is the conversion efficiency of solar cells?
- Most popular Silicon-based solar cells; structure and process
- Compound semiconductor-based solar cells
  1. What kind of materials are used in solar cells for space application?
  2. What is the CIGS solar cells?
  3. How to fabricate solar panels of CIGS?
  4. How to avoid the use of rare metals?
  5. What is perovskite type organic/inorganic solar cells?

Why solar cells now？

- Fossil fuels were brought about by blessing of sunshine in the ancient times.
- Urgent problem is the global warming by greenhouse gases
- We can no longer rely on Nuclear Power
- Renewable energy is blessing of nature.

Fossil Fuels were produced by the virtue of sunshine in the ancient times

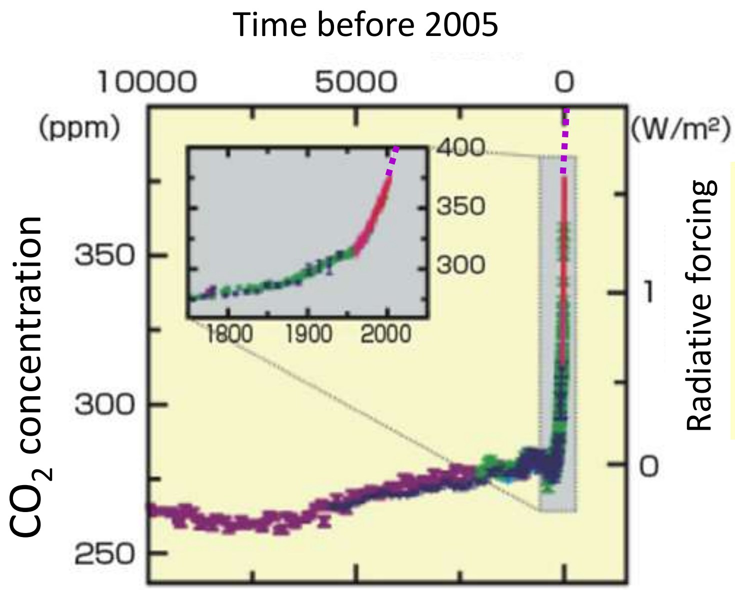
何億年も前の生物が化石燃料になったので、いわば化石燃料は太陽光の缶詰である



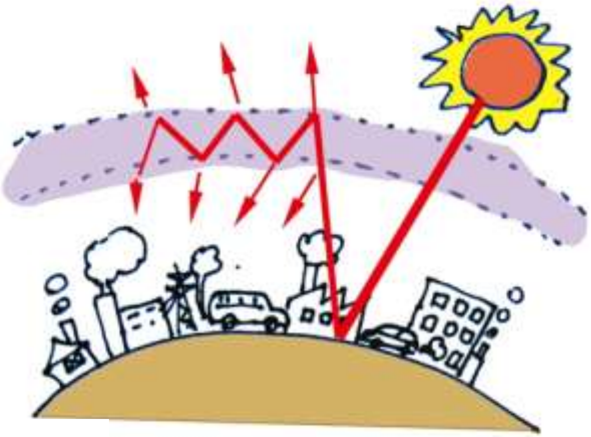
Thermal Power Station

Sunlight poured on the earth is finally absorbed ground or ocean to become heat, which produces wind and rain, nourish plats and animals to eat them. Withered plants and dead animals in the ancient times became coals and petroleum underground. These are the fossil fuels. We, human being constructed civilization by burning “blessings of ancient sunlight”.

Urgent! Global warming by greenhouse gases



10000 year change of oxygen concentration in atmosphere
Left axis means the radiative forcing reported by IPCC



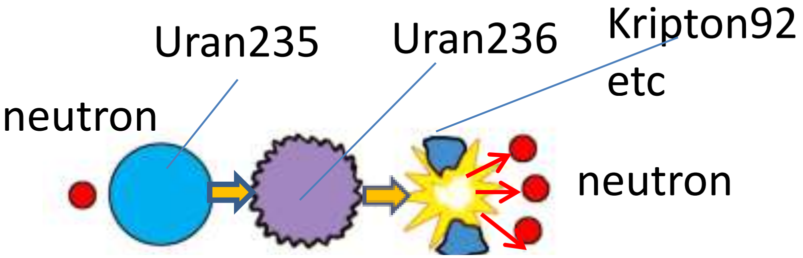
After 4th Report of IPCC, 2007

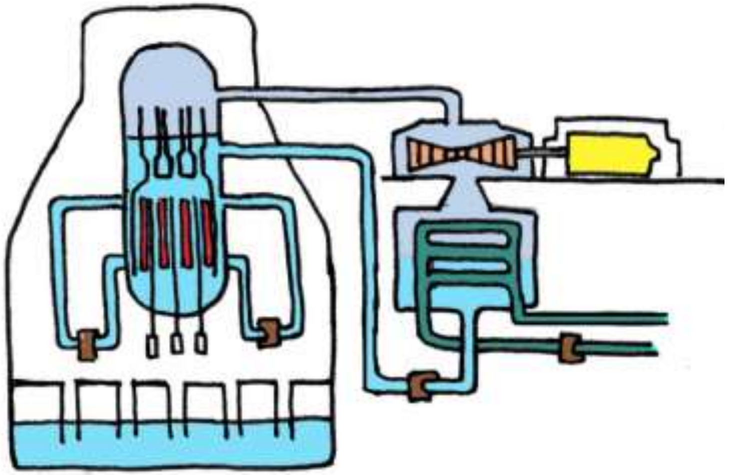
Eventually plenty of carbon dioxide was generated, which covers the atmospheric zone to increase the global temperature.

IPCC recently reported that the carbon dioxide concentration exceeded 400ppm for the first time.

The effect is called “global warming by greenhouse gases”.

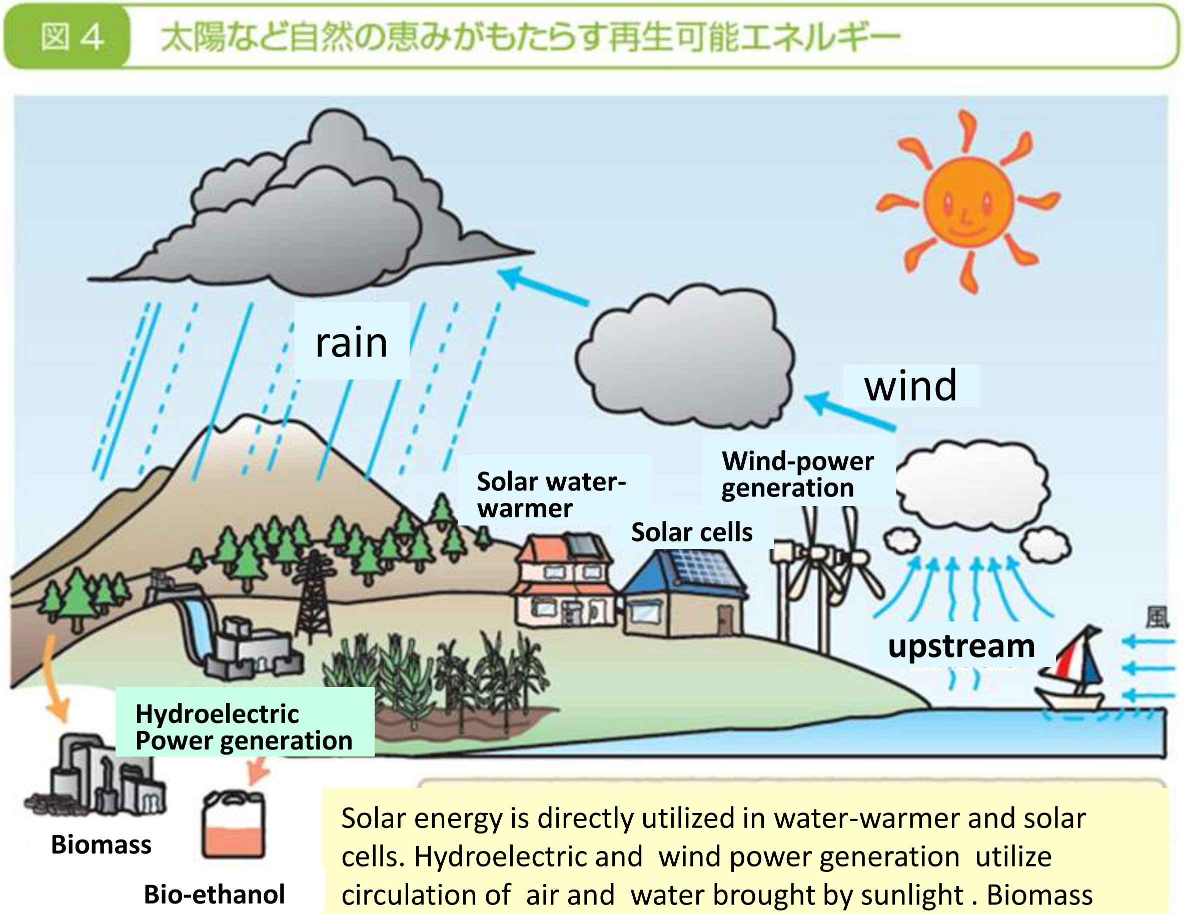
We can no longer rely on Nuclear Power





- Nuclear Power once attracted attention as a power which does not use fossil fuels.
- However, the meltdown of nuclear cores occurred after East-Japan Big Earthquake of March 11, 2011, nuclear generation is subjected to safety problem.
- Therefore, Japan can no longer rely on the Nuclear Power from now on.

Renewable energy is blessing of nature



Solar energy is directly utilized in water-warmer and solar cells. Hydroelectric and wind power generation utilize circulation of air and water brought by sunlight . Biomass and bio-ethanol utilize plants grown by virtue of sunshine.

We should produce energy using fossil fuels like coal and petroleum as small as possible.

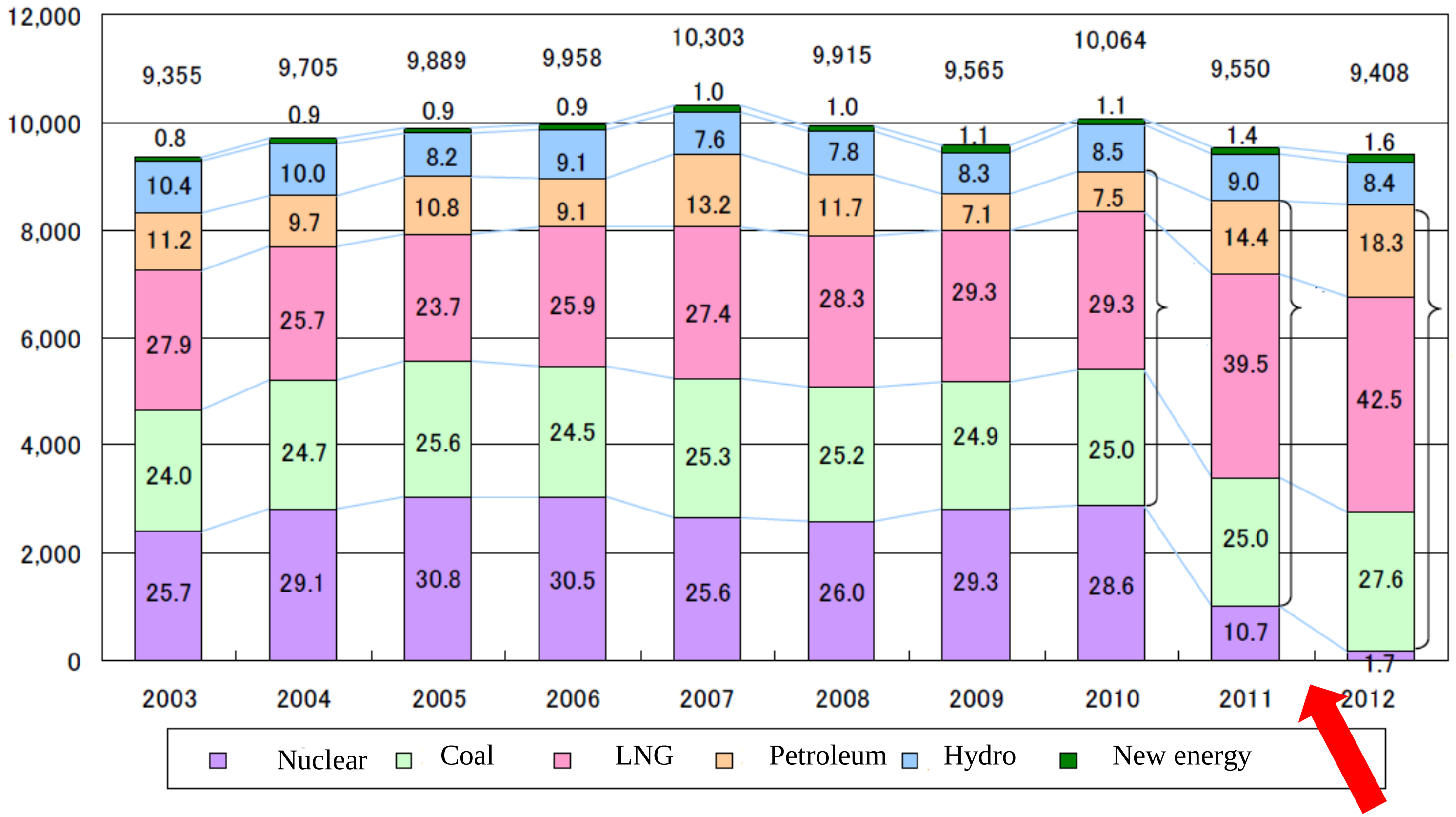
Therefore, diverse technologies to utilize various kinds of natural energy, such as water, wind, wave and sunshine.

The most important of them is solar energy.

Electric power generation in Japan.

(100 million kWh)

Renewable energy, accounted for 10.0% of Japanese power generation in FY2012; including 8.4% of hydraulic power.



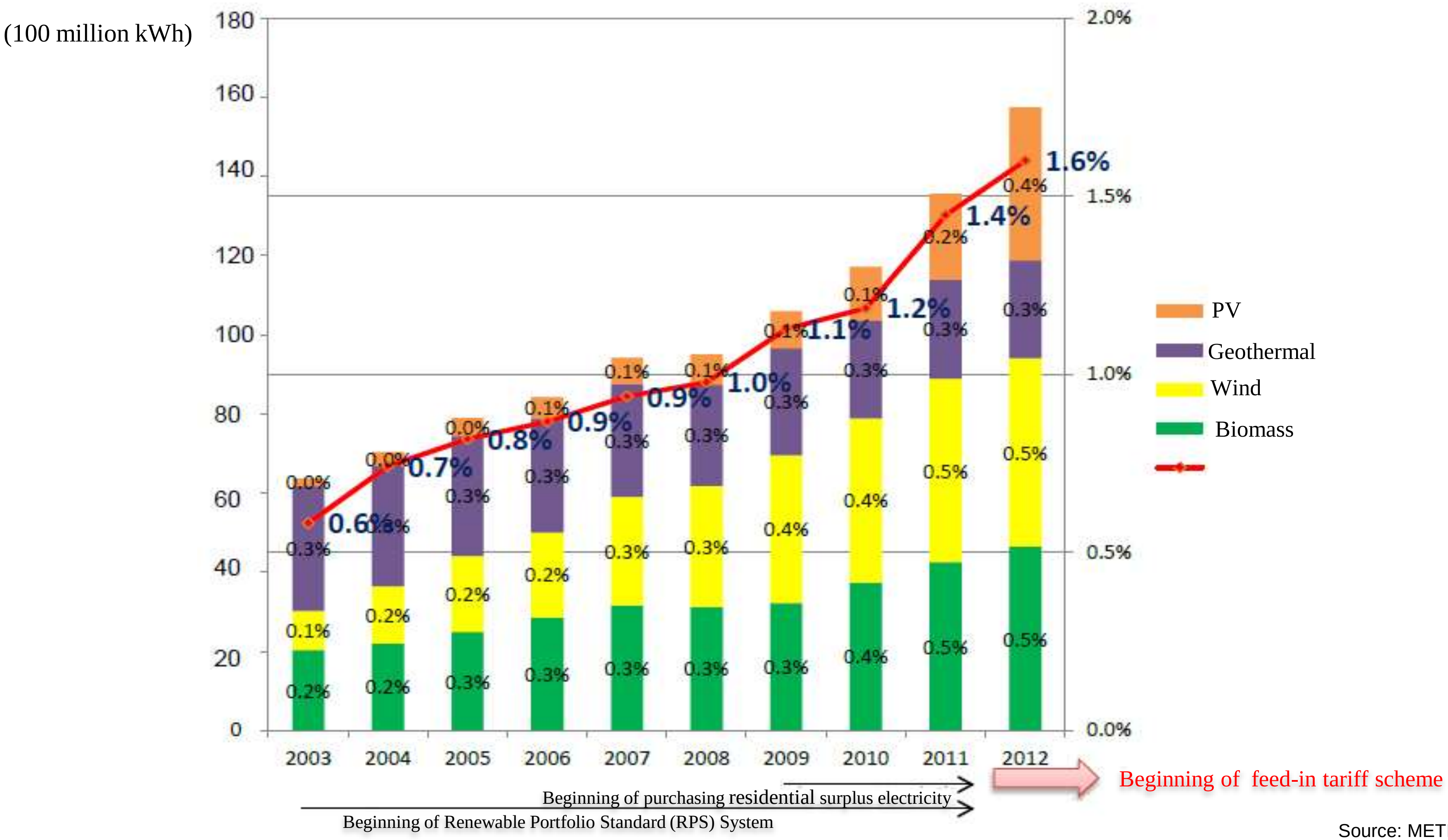
Fukushima Nuke Disaster

From the slides prepared by Atsuhiko Kiba
（NEDO） September 2, 2013

Source: METI

Long-term change in total supply from power-generating facilities of new energy except hydraulic power

- Since the introduction of the feed-in tariff scheme in 2012, the introduction of PV increased most.



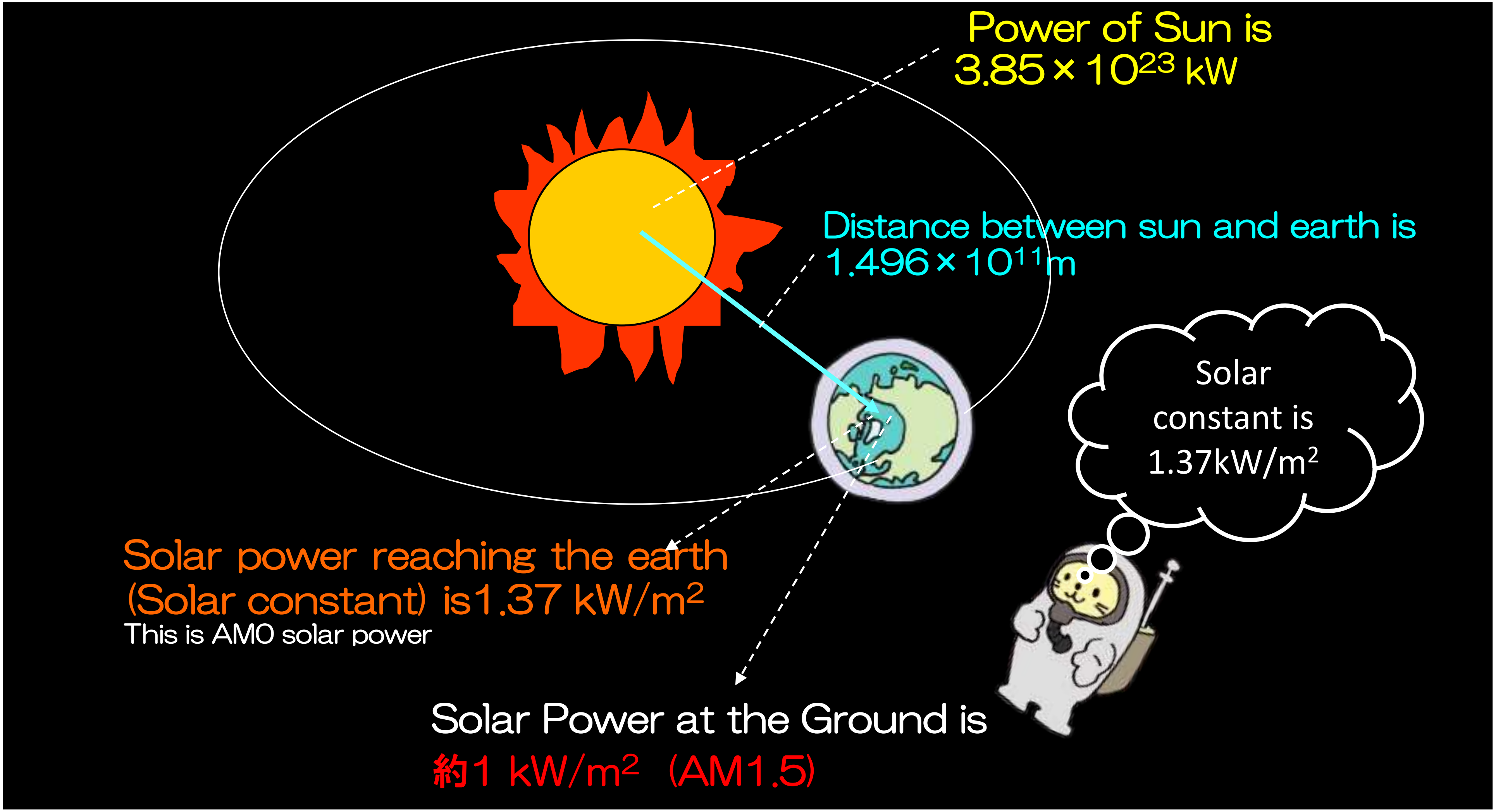
Source: METI

Situation of renewable energy introduction in 2014 FY

Category	Before FIT introduction	After FIT introduction		
	Cumulative total(-2012.6)	2012.7-2013.3	2013.FY	2014FY
Solar (Residential)	4.7GW	0.969GW	1.307GW	0.821GW
Solar (Non-residential)	0.9GW	0.704GW	5.735GW	8.572GW
Wind Power	2.6GW	0.063GW	0.047GW	0.221GW
Small Hydropower	9.6GW	0.002GW	0.004GW	0.083GW
Biomass	2.3GW	0.021GW	0.045GW	0.158GW
Geothermal	0.5GW	0.01GW	0	0.004GW
Total	20.6GW	1.769GW	6.381GW	9.86GW
		18.75GW		

After Whitepaper(2015FY) from Agency of Natural Resources and Energy under MITI

How much is the power of the sunshine per 1m^2?



Power of Sun is
3.85×10^{23} kW

Distance between sun and earth is
1.496×10^{11}m

Solar constant is 1.37kW/m^2

Solar power reaching the earth
(Solar constant) is1.37 kW/m^2
This is AM0 solar power

Solar Power at the Ground is
約1 kW/m^2 (AM1.5)

Small knowledge

Power vs. Energy

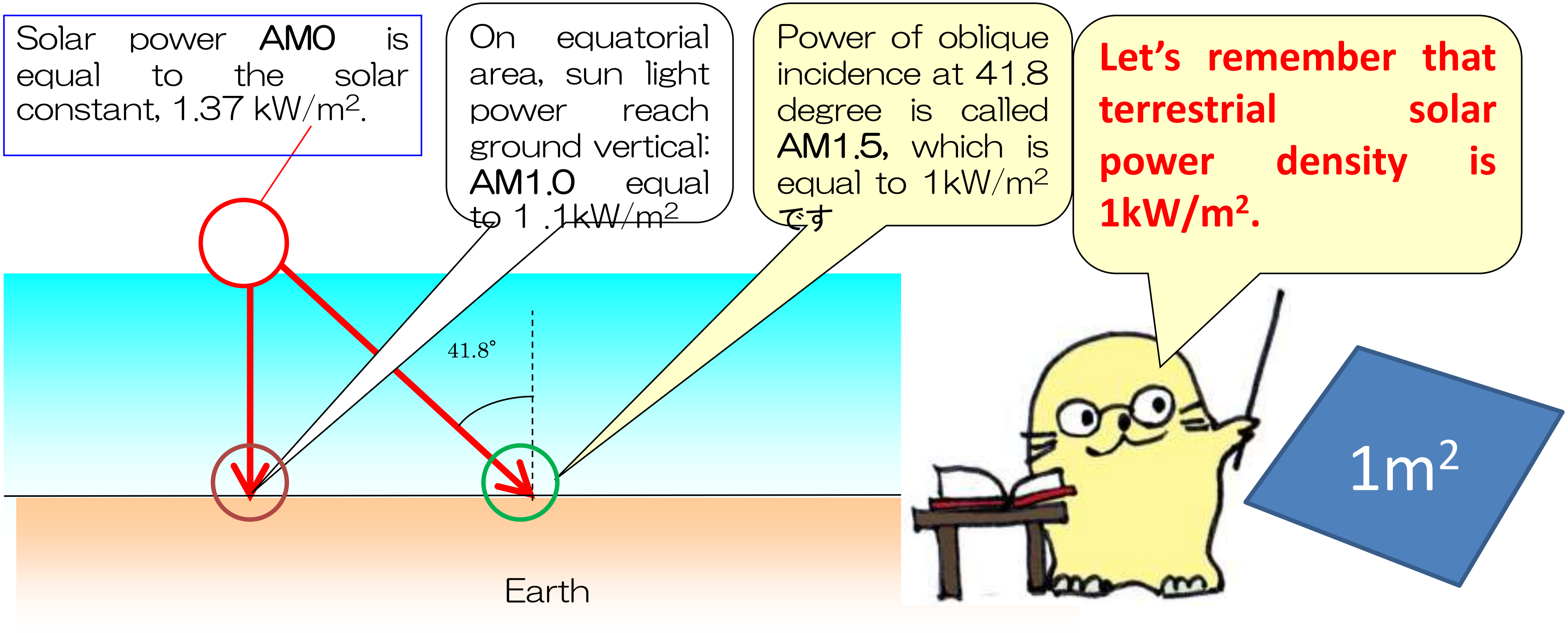
Power stands for an energy flow per unit time (1sec). Electric bulb of 100W consume 100J per second; W=J/s.

Energy flowing per area[$1m^2$], per time[1s]is called power density, the unit of which isW/m^2.

Product of power and time is energy. Energy consumed by 100W-electric bulb for 1 hour is 100Wh. Therefore 1Wh=3600J.

Solar Power at the ground; AM1.5

The air mass coefficient defines the direct optical path length through the Earth's atmosphere, expressed as a ratio relative to the path length vertically upwards, i.e. at the zenith. In the outer-space it is expressed as “AM 0”, while "AM1.5" is almost universal when characterizing terrestrial power-generating panels. Solar power density of AM-1.5 is **nearly 1kW/m^2**.



Solar power AM0 is equal to the solar constant, 1.37 kW/m^2.

On equatorial area, sun light power reach ground vertical: AM1.0 equal to 1 .1kW/m^2

Power of oblique incidence at 41.8 degree is called AM1.5, which is equal to 1kW/m^2 です

Let’s remember that terrestrial solar power density is 1kW/m^2.

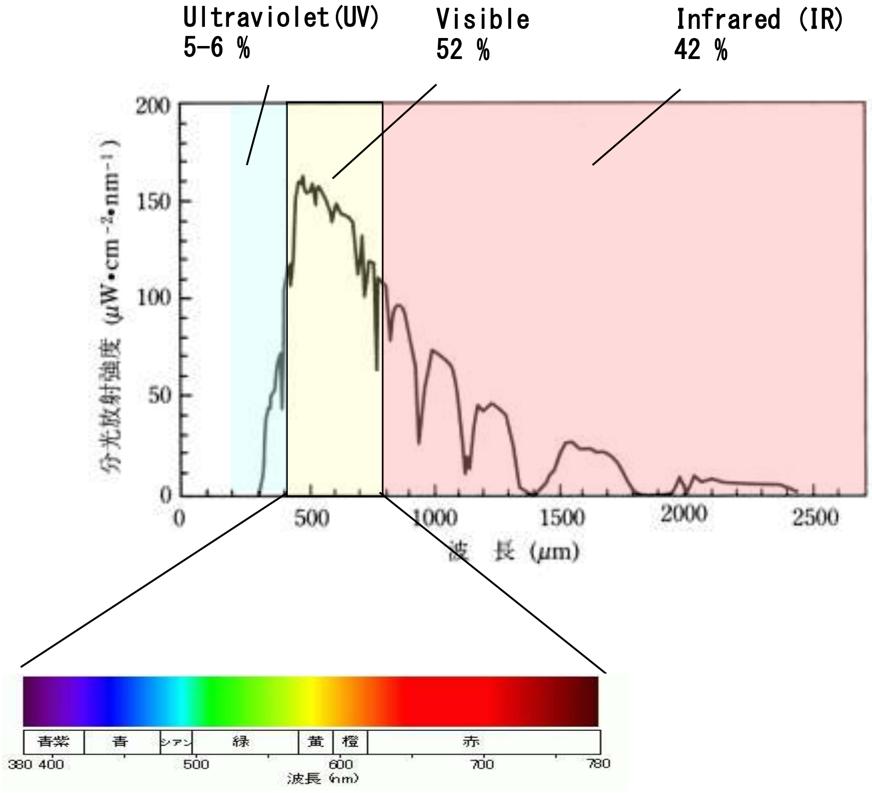
Can you tell the visible wavelength range of light?

―Solar Spectrum―

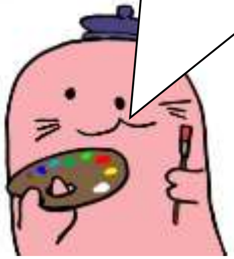
Visible wavelength range is 380nm to 780nm.

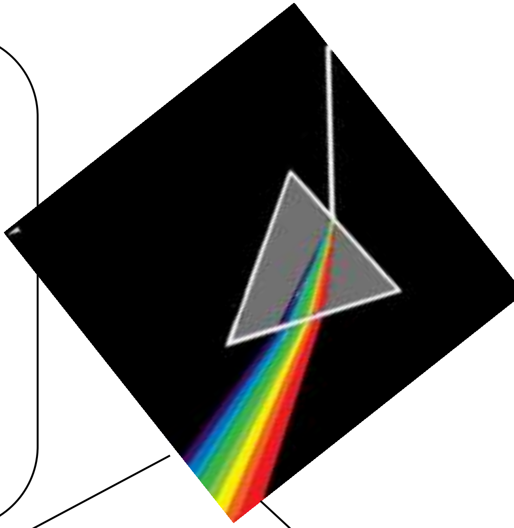
Terrestrial solar radiation spectrum (AM1.5)

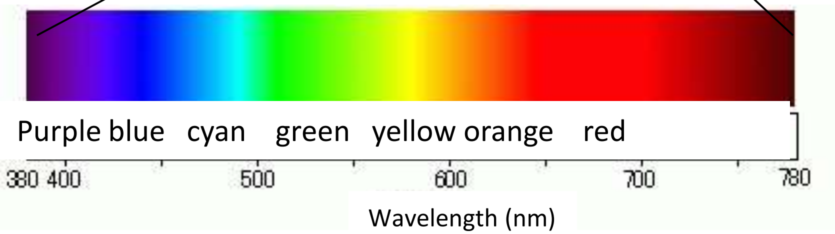
Invisible light



White sunlight is dispersed by prism to show a rainbow-like spectrum. Light with shorter wavelengths as purple and blue has higher energy than longer wavelengths.

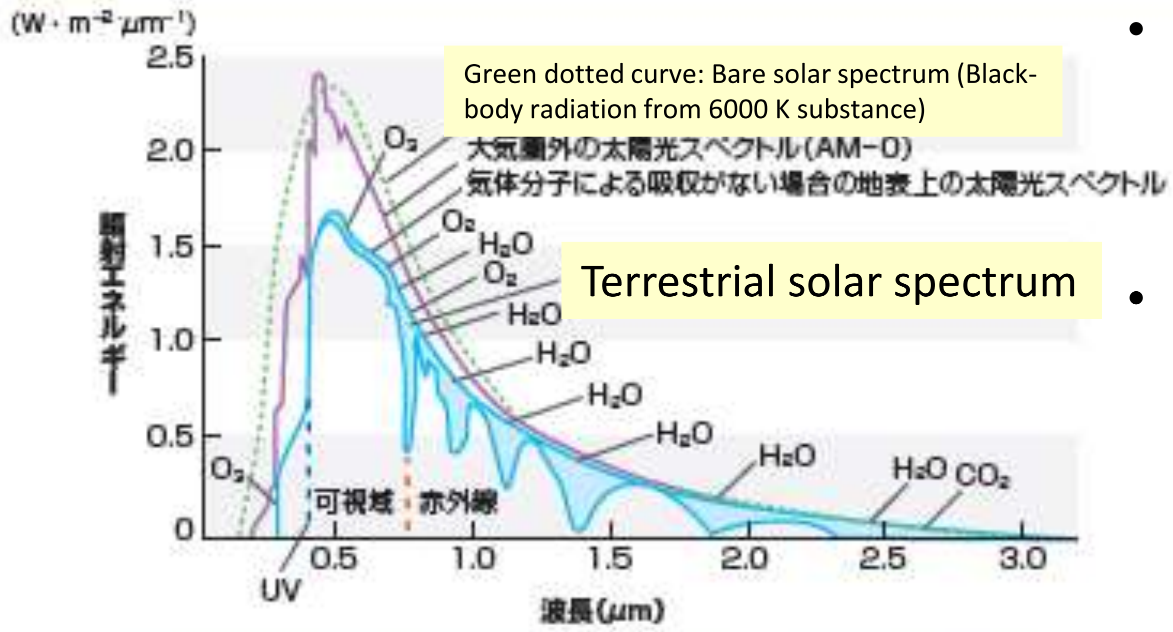






Why solar spectrum is so rough?

図2 大気を通過したときのスペクトルの落ち込み



Green dotted curve: Bare solar spectrum (Black-body radiation from 6000 K substance)

Terrestrial solar spectrum

Terrestrial spectrum is subjected to a number of dips due to absorptions by molecular vibrations of H2, O2 and CO2.

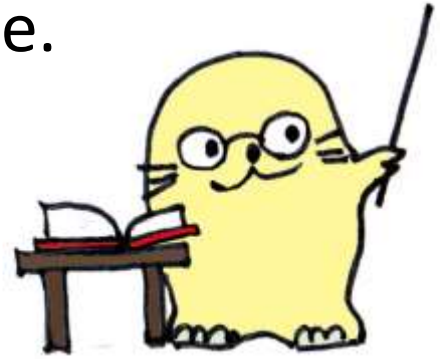
(参考：「太陽光発電入門」濱川圭弘 著、オーム社、1981年)

- By Rayleigh scattering wavelengths shorter than 1.0μm (visible to ultra-violet) are attenuated.
- In addition, due to absorption bands introduced by molecular oscillation of ozone (O3), water-vapor in air (H2O), oxigen（O_2）, carbon dioxide（CO_2）, the AM1.5 spectrum is subjected to a number of dips.

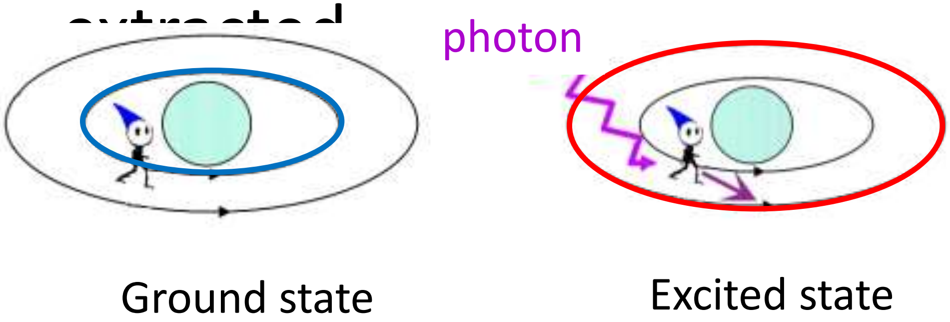
Why can we get electricity from solar irradiation?

Light is composed by a particle with an energy called photon. A photon with a frequency *ν* has an energy expressed by *E*=*hν*.
（*h* is Planck constant）

Absorption of a photon by a substance gives energy to an electron in the substance to be in the excited state.



Electricity may be obtained if the energy of the excited electron is extracted

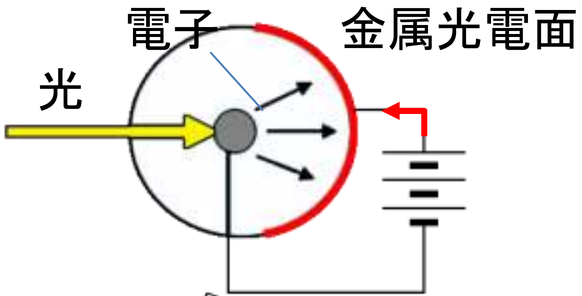


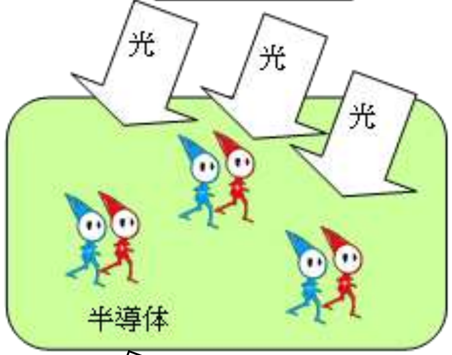
- Photon energy E of the light with a wavelength λ is can be expressed by E(eV)=hc/λ=1239.8/λ(nm) where ν=c/λ is applied.

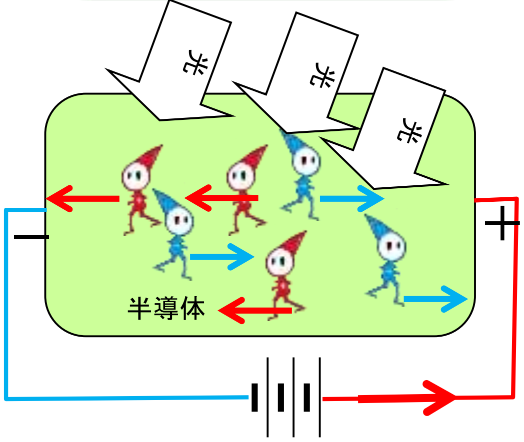
What occurs if metals and semiconductors are irradiated?→ Photoelectron effects

Light-irradiated metals emit electrons into vacuum by external photoelectron effect (photelectron emission). However, electric current never flows unless high voltage is applied. Therefore this effect cannot be used for power generation.

Light-irradiated semiconductors produce electron-hole pairs by internal photoelectron effect (photoconductivity). Current cannot be obtained unless external voltage is applied.
This effect can be used as a photo-switch, but cannot generate power.

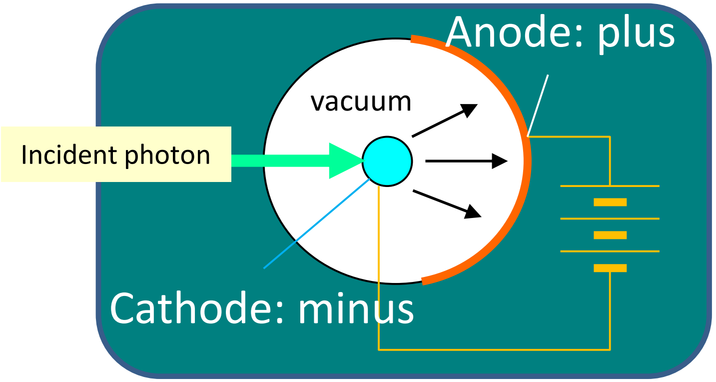






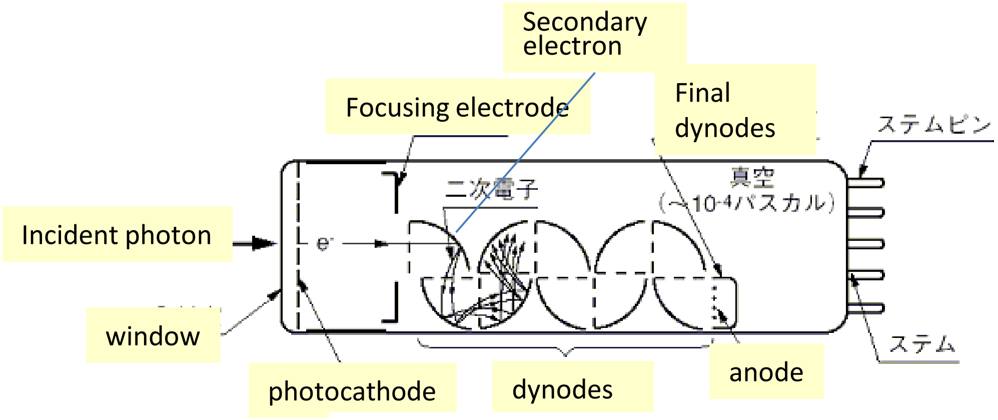
Photoemission

Vacuum Tube called “Photoelectron tube”
   Light-irradiated metal: negative
   Opposing anode metal: positive



If metal is irradiated by light in vacuum, photoelectrons are emitted from the metal and are attracted by the positive charge on the anode, only if the photon energy exceeds the work-function of the metal.

Various photomultiplier tubes



Schematic illustration of a Photomultiplier

Application of Photomultiplier

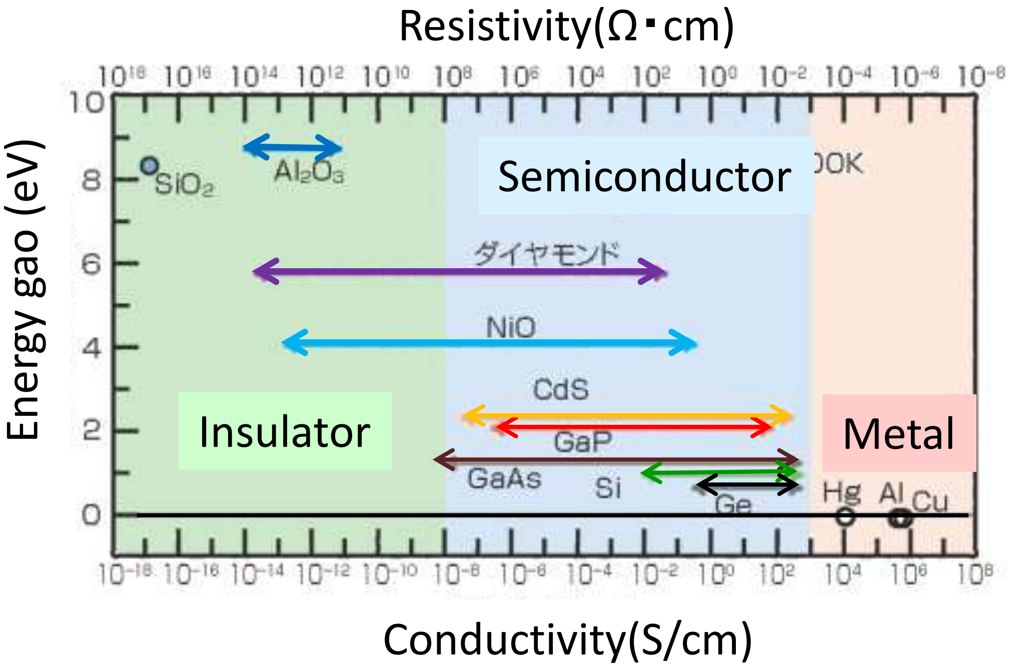
At the Super-Kamiokande facility, researchers are capturing neutrino arriving to the earth from the space. Neutrino traversing the water vessel often collides with some charged particle to emit weak light called Cherenkov radiation.

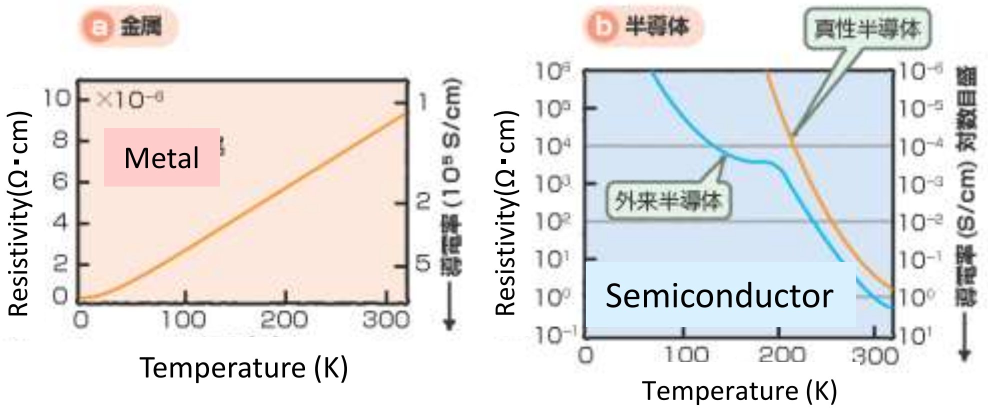
Photomultipliers convert the weak light to electron and are multiplied to output photo-voltage.

Total of 11200 world-largest photomultiplier tubes of 50 cm in diameter. The photomultiplier is so sensitive that it can detect the light of flashlight emitted from the moon to the earth.

http://www-sk.icrr.u-tokyo.ac.jp/sk/intro/index_j.html

Semiconductors？

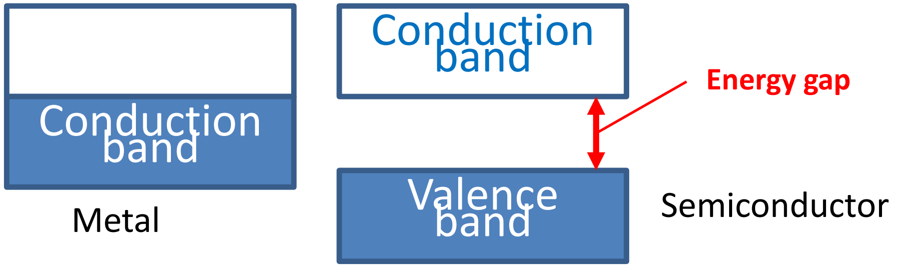




Semiconductor is a material, the resistivity of which takes an intermediate value between conductor (metal) and insulator.

The resistivity of semiconductor exponentially decreases with temperature, while that of metal increases with temperature.

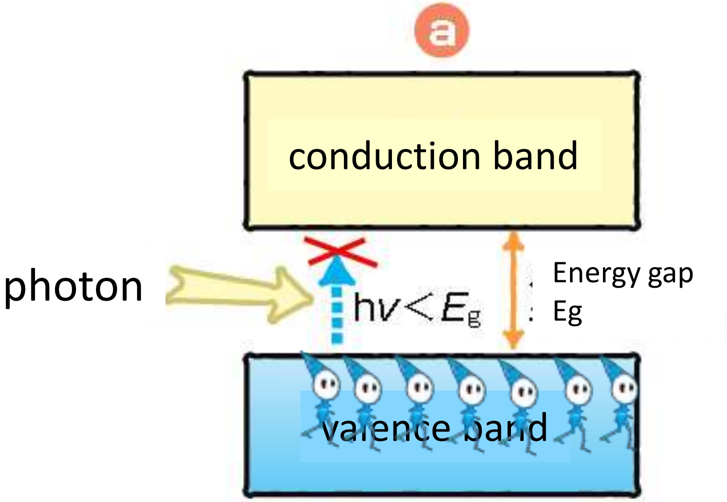
The temperature-dependence of the semiconductor is caused by the energy gap of the semiconductor.

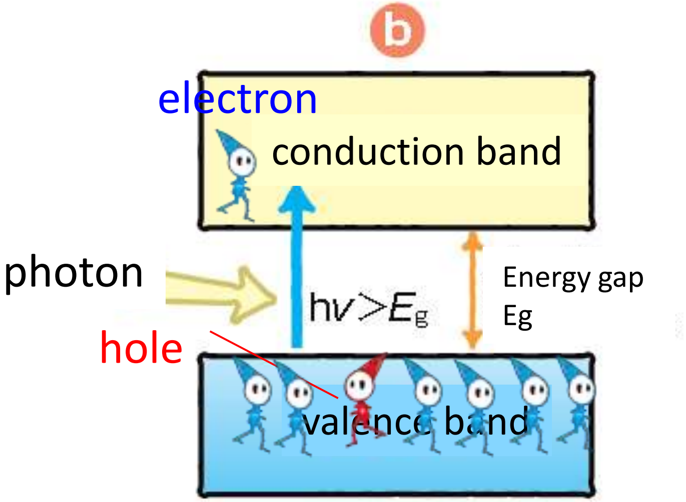


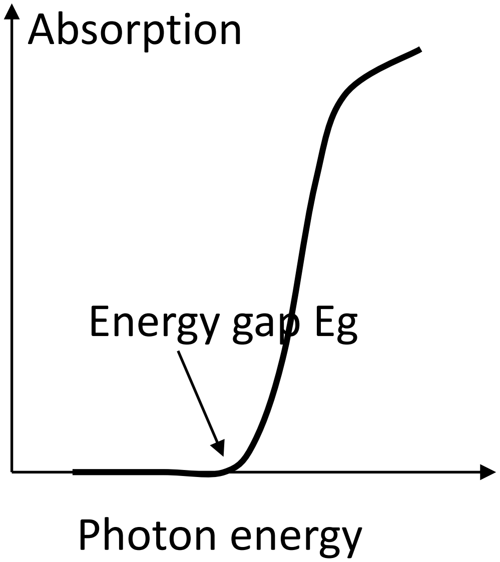
Energy gap of Semiconductor and Optical Absorption

If the incident photon energy（*hv*）is below the energy gap （*E*g） as shown in Fig. a, valence electron cannot be excited to the conduction band, and the semiconductor does not absorb light.

On the other hand, if *hv* exceeds as in Fig.b, *E*g valence electron can be excited to the conduction band by the photon energy, and the semiconductor absorbs the light.



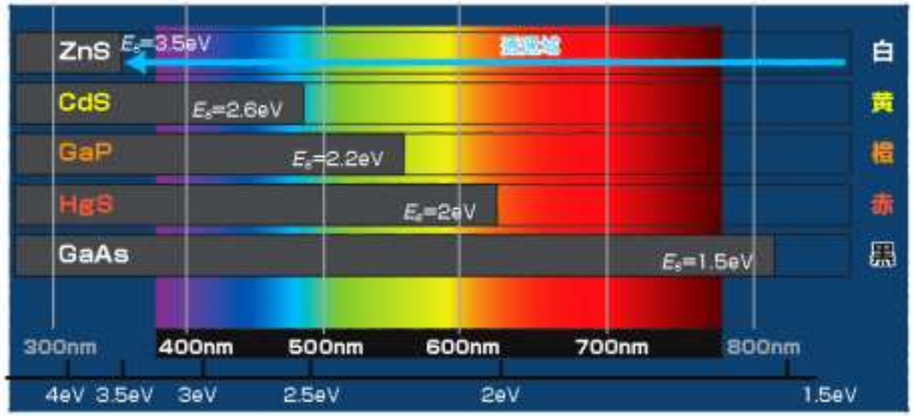


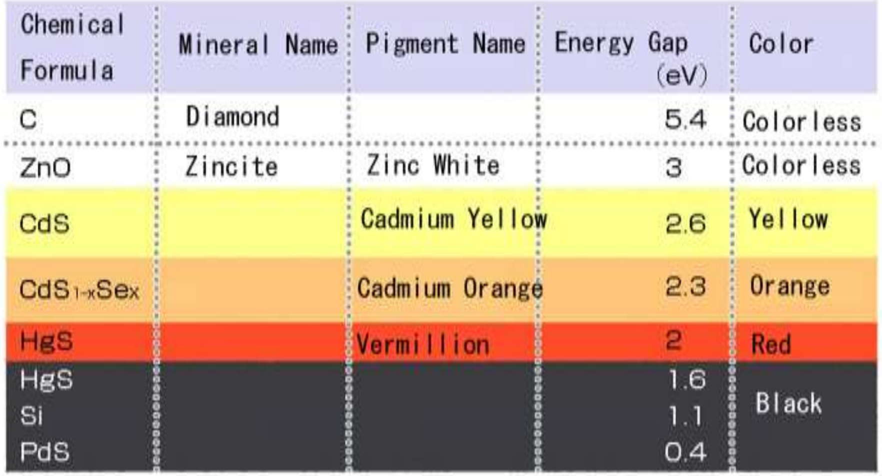


Energy gap and color of semiconductor

Figure shows relation of the enegy gap and color of the crystal in different semiconductors.

- Zinc sulfide（ZnS）is colorless transparent, since all visible wavelengths can go through ZnS owing to the wide gap of 3.5 eV, which means only wavelength shorter than 354 nm is absorbed. The powder of ZnS is white due to multiple scattering of transmitted light.
- Cadmium sulfide（CdS）is yellow in color, since light with wavelength shorter than 477 nm (corresponding to energy gap of $Eg = 2.6$eV) is absorbed leaving red to green wavelengths transmit.
- Gallium phosphide（GaP）is orange in color, since wavelengths shorter than 564nm (corresponding to $Eg = 2.2$eV) are absorbed and red-to-yellow light transmits.
- Mercury sulfide (HgS) is red, since Eg is 2eV.





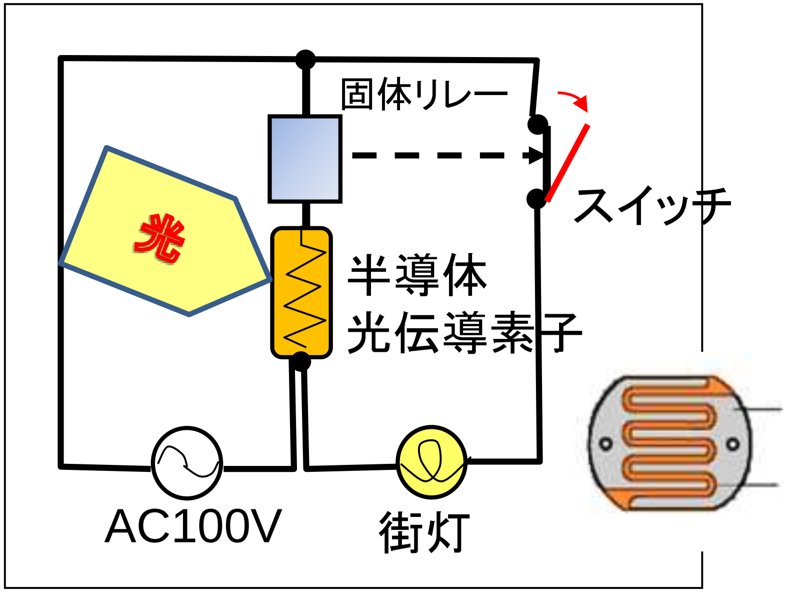
Chemical Formula	Mineral Name	Pigment Name	Energy Gap (eV)	Color
C	Diamond		5.4	Colorless
ZnO	Zincite	Zinc White	3	Colorless
CdS		Cadmium Yellow	2.6	Yellow
$CdS_{1-x}Se_x$		Cadmium Orange	2.3	Orange
HgS		Vermillion	2	Red
HgS Si PdS			1.6 1.1 0.4	Black

Photoconductivity

How Street Lamps are Lit Automatically in Evening?

Street lamps are lit automatically in the evening. For this purpose semiconductor photoconductive devices are utilized

In daytime by a light illumination resistivity of semiconductor photoconductive element becomes decreased to switch off the lamp circuit by a solid state relay. In the darkness the resistivity increased which switch on the circuit of lamp.

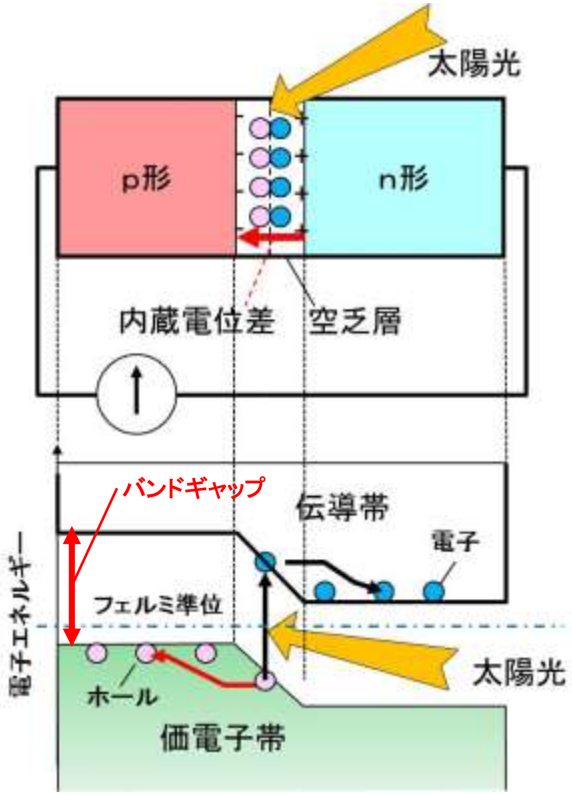


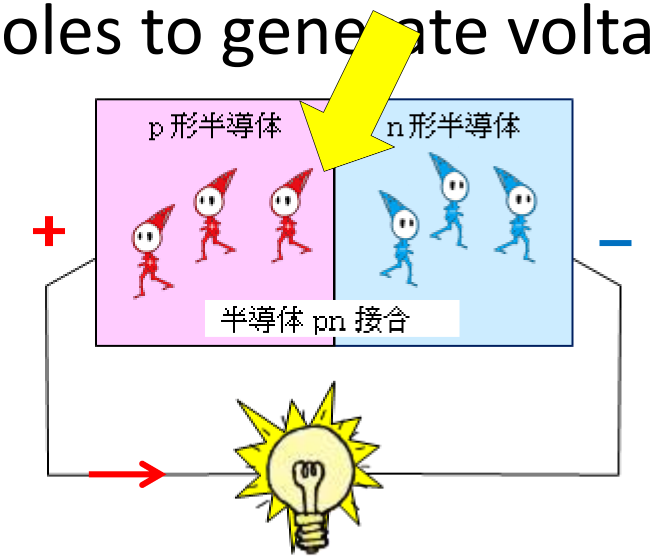
Semicoductor only work as a switch and never generate the power,

To generate power a semiconductor device is necessary

Ptovoltage can only be obtained when pn-junction diode is prepared.

A potential slope is formed at the interface of p-type and n-type semiconductors, which effectively separates photo-generated electrons and holes to generate voltage.



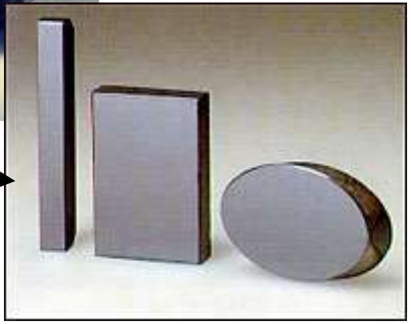


Various Semiconductors for Solar Cells

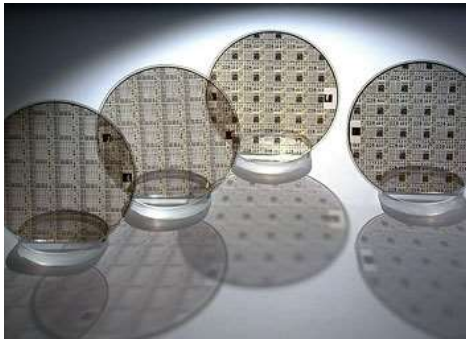
- Silicon(Si)
- Gallium arsenide(GaAs)
- Gallium nitride(GaN)
- Cadmium telluride (CdTe)
- Cadmuin sulphide (CdS)

silicon

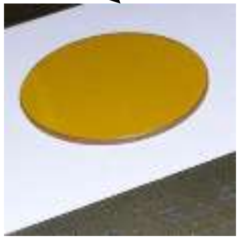
Gallium arsenide



GaN



CdTe



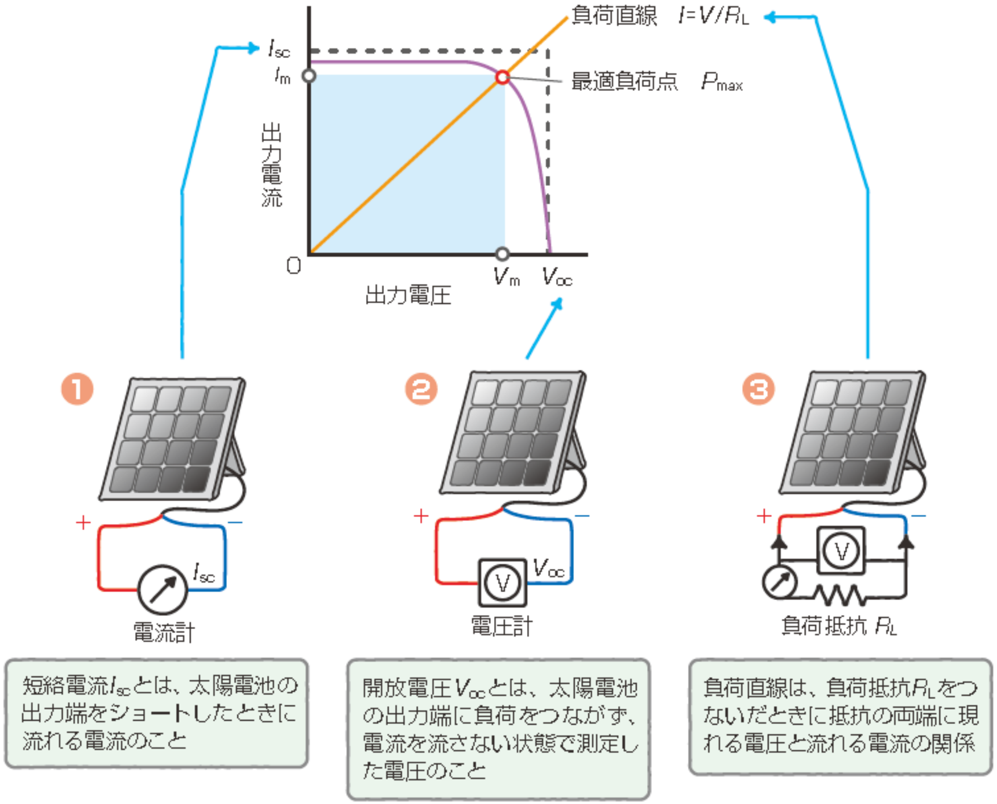
CdS

http://www.iaf.fraunhofer.de/index.htm

LPCBC INSTITUTE OF SOLID STATE PHYSICS,
RUSSIAN ACADEMY OF SCIENCES

Definition of Efficiency

Conversion efficiency is a measure for evaluation of solar cells to indicate how much electric power can be obtained from the solar power.



短絡電流I_{sc}とは、太陽電池の出力端をショートしたときに流れる電流のこと

開放電圧V_{oc}とは、太陽電池の出力端に負荷をつながず、電流を流さない状態で測定した電圧のこと

負荷直線は、負荷抵抗R_Lをつないだときに抵抗の両端に現れる電圧と流れる電流の関係

The graph presents a relation between output voltage and output current, in which Isc means short-circuit current, i.e., a current flowing when output terminal is terminated by an ammeter as illustrated in ❶. While Voc means open-circuit voltage, i.e., output voltage without any load as illustrated in ❷.

The maximum power capable to obtain is smaller than the dotted area Voc × Isc, because the voltage-current relation is rounded as shown by the red curve.

The orange line express the relation **I=V/RL** when the solar cell is loaded with a resistance RL as shown in ❸.

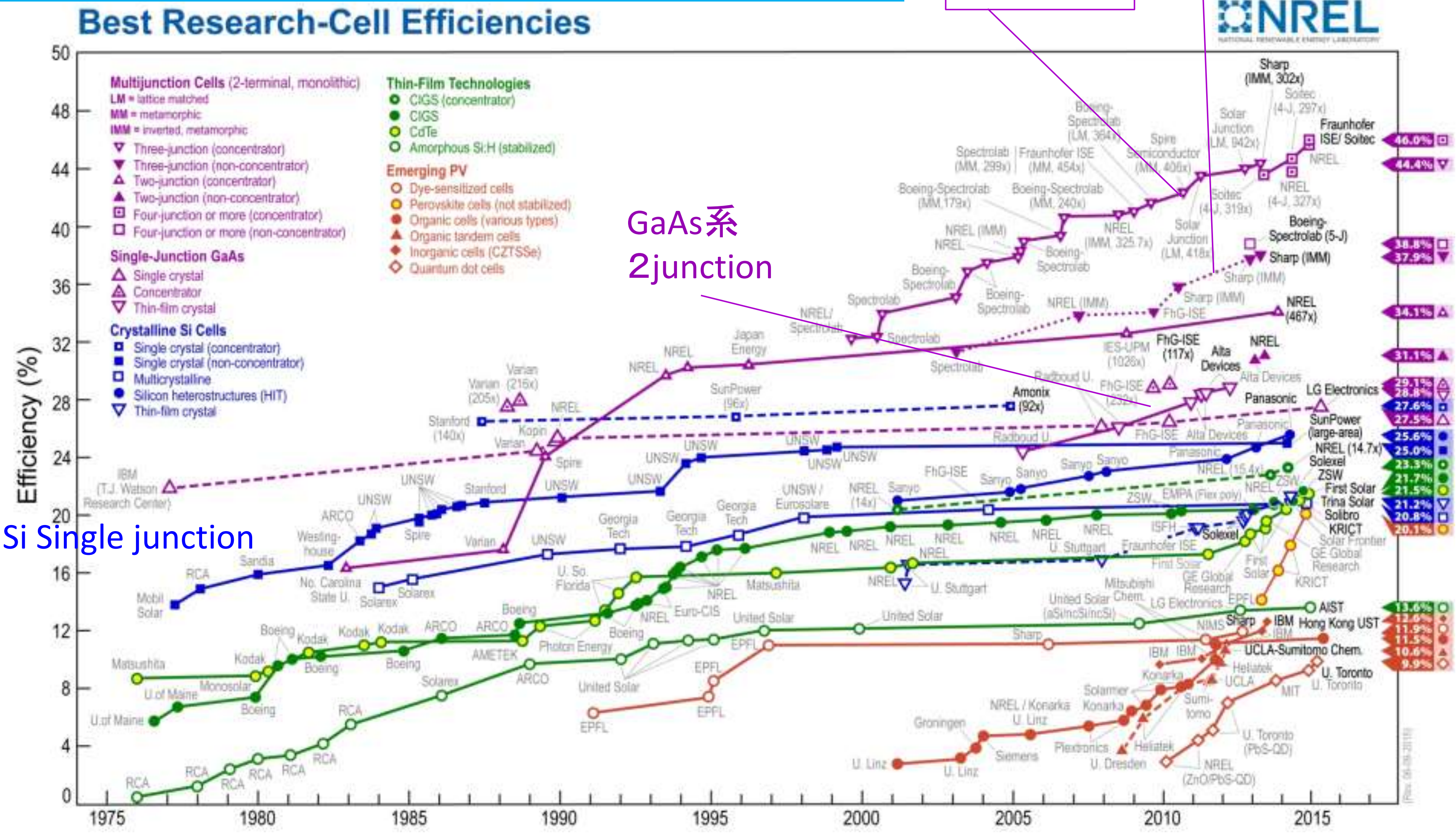
Maximum output power Pmax can be expressed by an area of the largest square inscribed in the I-V curve at the crossing point of load line and the curve.

The conversion efficiency η is expressed by the percentage ratio of Pmax to the terrestrial solar power (1kW/m2 times illuminated area).

Conversion Efficiency of Practical Solar Cells

- The champion efficiency of Si cell is 25.0% (UNSW;1cm^2) for small area, and 22.7% for large-area module. HIT type shows 25.6% (Panasonic;144cm^2)←2014.4.10
- Efficiency of GaAs-based multi-junction cell is 44.4%(Sharp;concentrated 0.16cm^2)←2013.6.14、and 35.8%(Sharp;unconcentrated). It is 36.1% for large area module.
- For CIGS-based cell, the efficiency is 20.9%(Solar Frontier, small area), 17.8%(small module), 13.6%(large area)

Best Research-Cell Efficiencies



GaAs-based 3junction

Concentrated

Non-concentrated

GaAs系 2junction

Si Single junction

Theoretical Limitation

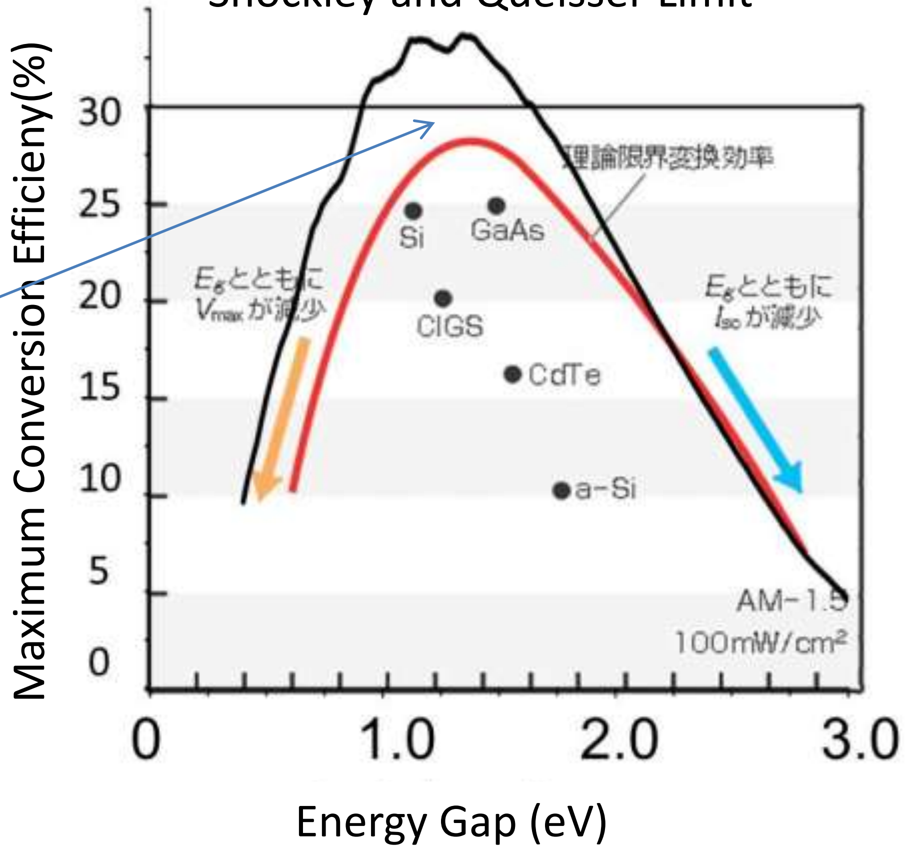
Conversion efficiency is a fuction of energy gap of the semiconductor. Existence f a theoretical limit is predicted by Shockley and Queisser, as shown by the black curve in the Figure. For lower Eg side Vmax decreases with decrease of Eg, while for higher Eg side Isc decreases with increase of Eg, which introduces a maximu at about Eg=1.4 eV.

Therefore, efficiency of single junction cell is no more than 30%.

Theoretical limit of Si solar cell efficiency is 27%, while realized maximum reaches 25%. Therefore there is only a small room to be improved.

On the other hand, maximum realized efficiency of the CIGS cell is 20%, there is a room to be improved to theoretical limit of 28%.

Shockley and Queisser Limit



Comparison of Solar Cells

表 1 太陽電池の比較

materials	type	Conversion efficiency (%)		Module cost US$/W	Resource	Feature
		module	cell			
Si-based	Single crystal	22.9	25.0	1.1	△	高い変換効率。安定。Si 材料の多消費に難
	multicrystalline	19.5	20.4	1.08	△	比較的高効率、普及。材料供給に難
	Thin Film	8,2	10.8	0.84	○	低コストで大面積可能。省資源。低効率と光劣化に難
Compound-based	Ⅲ－Ⅴ族	38.5	44.4	concentrated	△	超高効率。宇宙用。高コスト、資源問題に難
	CIGS系	17.8	20.9	(0.99)$^{\&}$	○	低コストで大面積可能。省資源。大面積効率に難
	CdTe系	16.1	19.8	0.98^{+}	△	低コスト、大量生産。中効率。Cd 使用が問題
Chemical	DSS	8.9	11.9	(0.75－3.3)$^{\#}$	○	低コスト、省資源。中効率。液体使用が難。光劣化も
	Organic cell	6.8	10.7	(1－2.84)$^{\#}$	○	低コスト、省資源。中効率
	perovskite		20		○	

In Table 1 are listed Cell- and Module-efficiency, Cost, Resources, and features of diverse solar cells.

Multicrystalline Si Module shows fairly high efficiency and low cost and reliable, thanks to long history of research.

Most of popular solar modules for home roofs are of this type.

＊2010年12月の最低価格(http://www.solarbuzz.com/Moduleprices.htm)
& 2008年：Nanosolar 社の発表(role-to-role)
＋2009年：First Solar 社発表

Estimation: Joseph Kalowekamo, Erin Baker : Estimating the manufacturing cost of purely organic solar cells; Solar Energy 83, 1224-1231 (2009)

**M.Green et al., Solr cell Efficiency tables (version 43)
Prog Photovolt. ReAppl. 2014 22, 1-9s.

＊＊＊ピークパワー1Wあたりのモジュールコストを米ドルで表したもの

種々の太陽電池のセル変換効率・モジュール変換効率のチャンピオンデータ(2010年時点)および記載のあるモジュールコスト＊＊＊の一覧表

Cell-Module-Array

Open-circuit voltage is determined by semiconductor species and is less than 1 V.

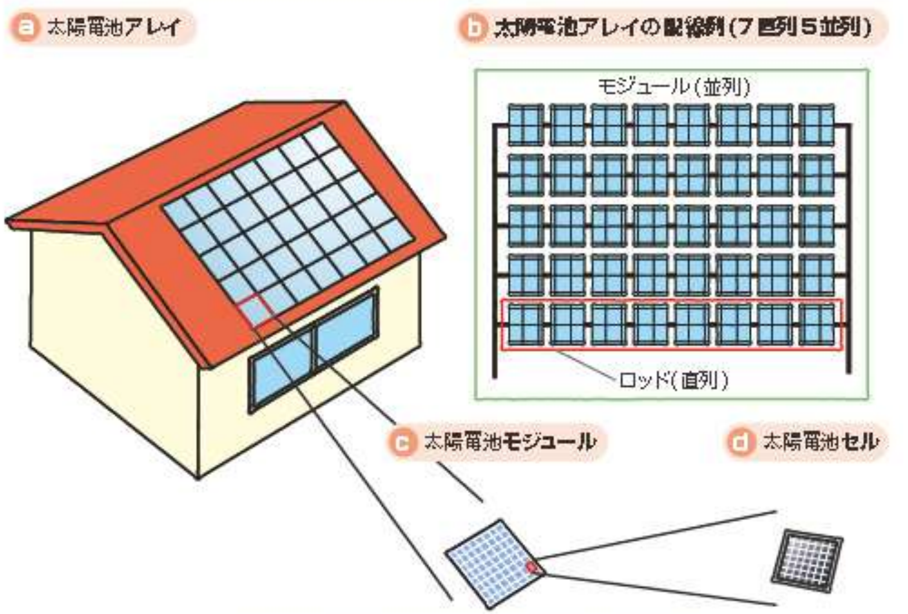
A sub-module with 25 series-connected cells show an output of around 20V.

An output voltage of a module with 7 series-connected submodules is nearly 150V.

To get larger output current an array of 7 series and 5 parallel modules is constructed.

The output power of this array solar panel is approximately 3 kW.

図1　太陽電池モジュールと太陽電池アレイ



太陽電池セルを直列につないだものがモジュール、
モジュールを直並列につないだものがアレイ

Conversion Efficiency of Practical Modules

Electrical power per $1m^2$ is 128W for multicrystalline Si module, and 136W for single crystal Si module. Since solar power per $1m^2$ is approximately 1kW, practically about 13 to 15%of solar power is converted to electricity.

HIT solar cell module, which is a hybrid of crystalline and thin film types, generates electric power per $1m^2$ as large as 152W.

Efficiency decrease in module from cell is due to following reasons;

❶ gap between cells , ❷ shaded area under electrodes, ❸ area decrease by frames

Multicrystalline Si

Area: 1650 x 995 mm2
Max output: 210 W

Single crystal Si

Area: 1318 x 1004 mm2
Max output: 180 W

HIT type

Area: 1320 x 895 mm2
Max output: 180 W

InGaP/InGaAs/Ge solar module with 35% efficiency was installed in Tokai Univ Solar Car.

information

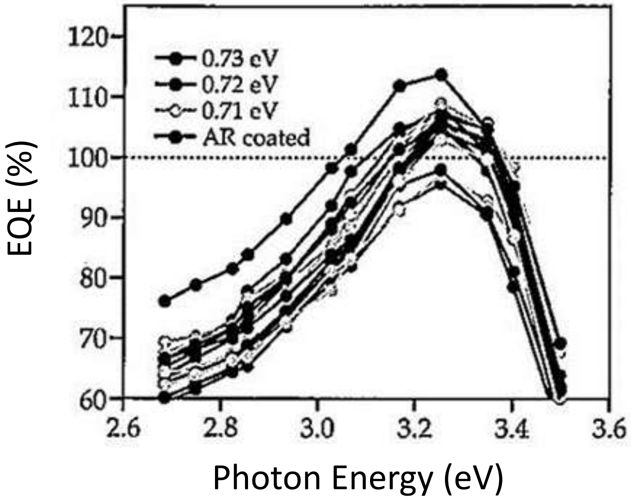
Quantum Efficiency

A solar cell's quantum efficiency value indicates the amount of current that the cell will produce when irradiated by photons of a particular wavelength.

External Quantum Efficiency (EQE) is the ratio of the number of charge carriers collected by the solar cell to the number of photons of a given energy shining on the solar cell from outside (incident photons).

Internal Quantum Efficiency (IQE) is the ratio of the number of charge carriers collected by the solar cell to the number of photons of a given energy that shine on the solar cell from outside and are absorbed by the cell.

High QE does not necessary mean high conversion efficiency, due to voltage loss at the output.



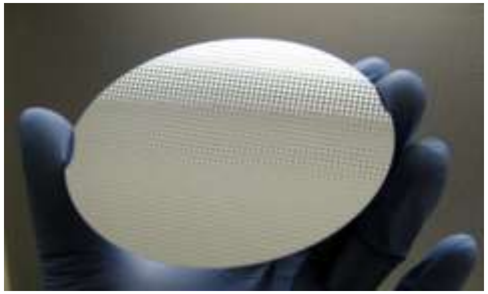
Although EQE of nano-crystal quantum dot cell exceeds 100%, obtained conversion efficiency is far below theoretical limit.

Johanna L. Miller: Multiple exciton generation enhances a working solar cell
Physics Today 65 (2) pp17-19 (2012) Feb 2012

SILICON SOLAR CELLS AND MODULES

Preparation of Silicon Crystals

1. Silica to Metallic Silicon
2. Metallic Silicon to High Purity (eleven nine) Polycrystalline Silicon
3. Polycrystal to Single crystal (Ingot) (CZ or FZ)
4. Ingot to Wafer by slicing and polishing

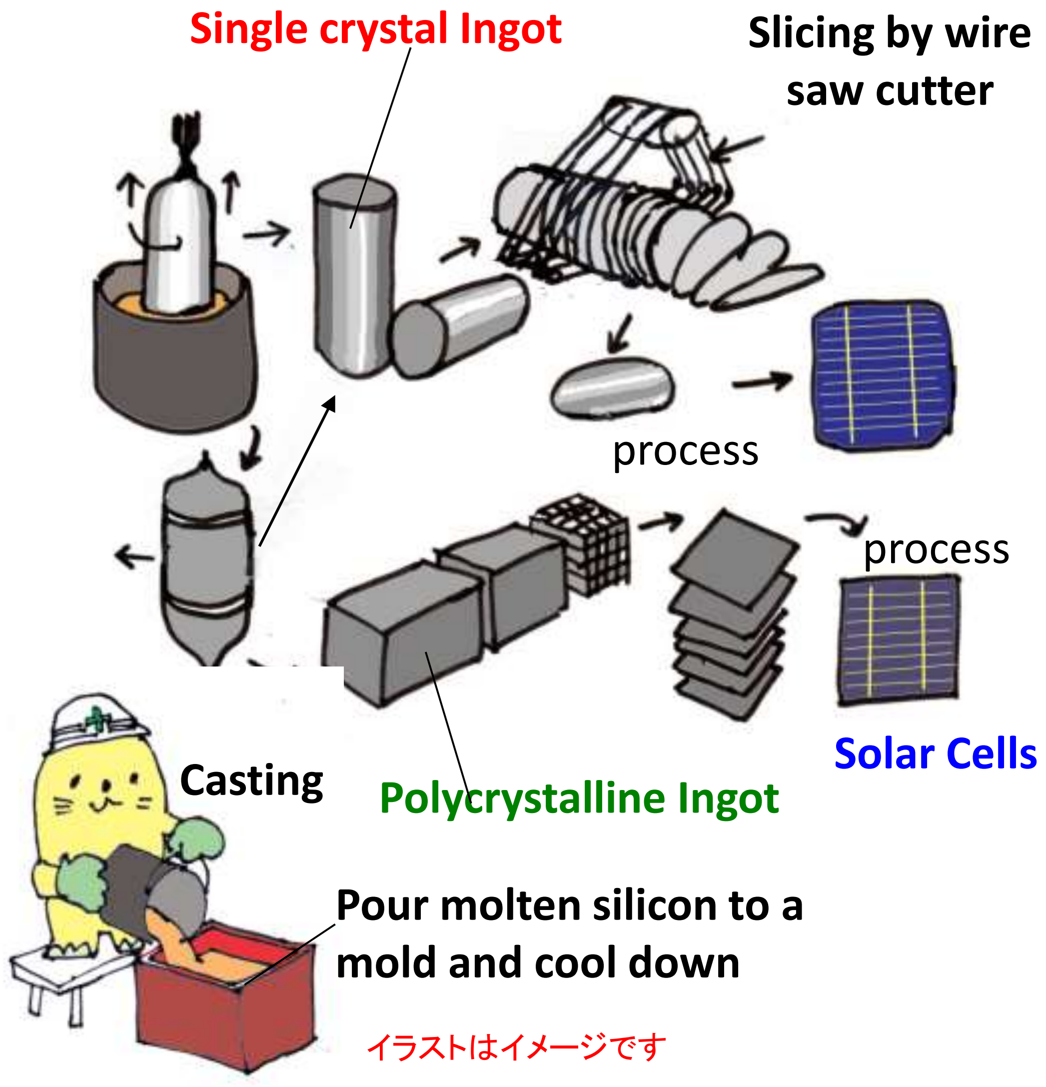


http：www.um.u-tokyo.ac.jp/.../ SILICON/HOME.HTM

Processes for Silicon Solar Cells

Single Crystal Type : Single crystal ingot is sliced by using wire-saw cutter. Wafers are sent to the cell-forming process (impurity diffusion to form pn-junction and electrode deposition).

Multicrystalline Type : Edge portion of single crystals and scraps due to Kerf losses are molten and casted to multicrystalline ingot. The ingot is sliced to wafers and is subjected to form solar cells.



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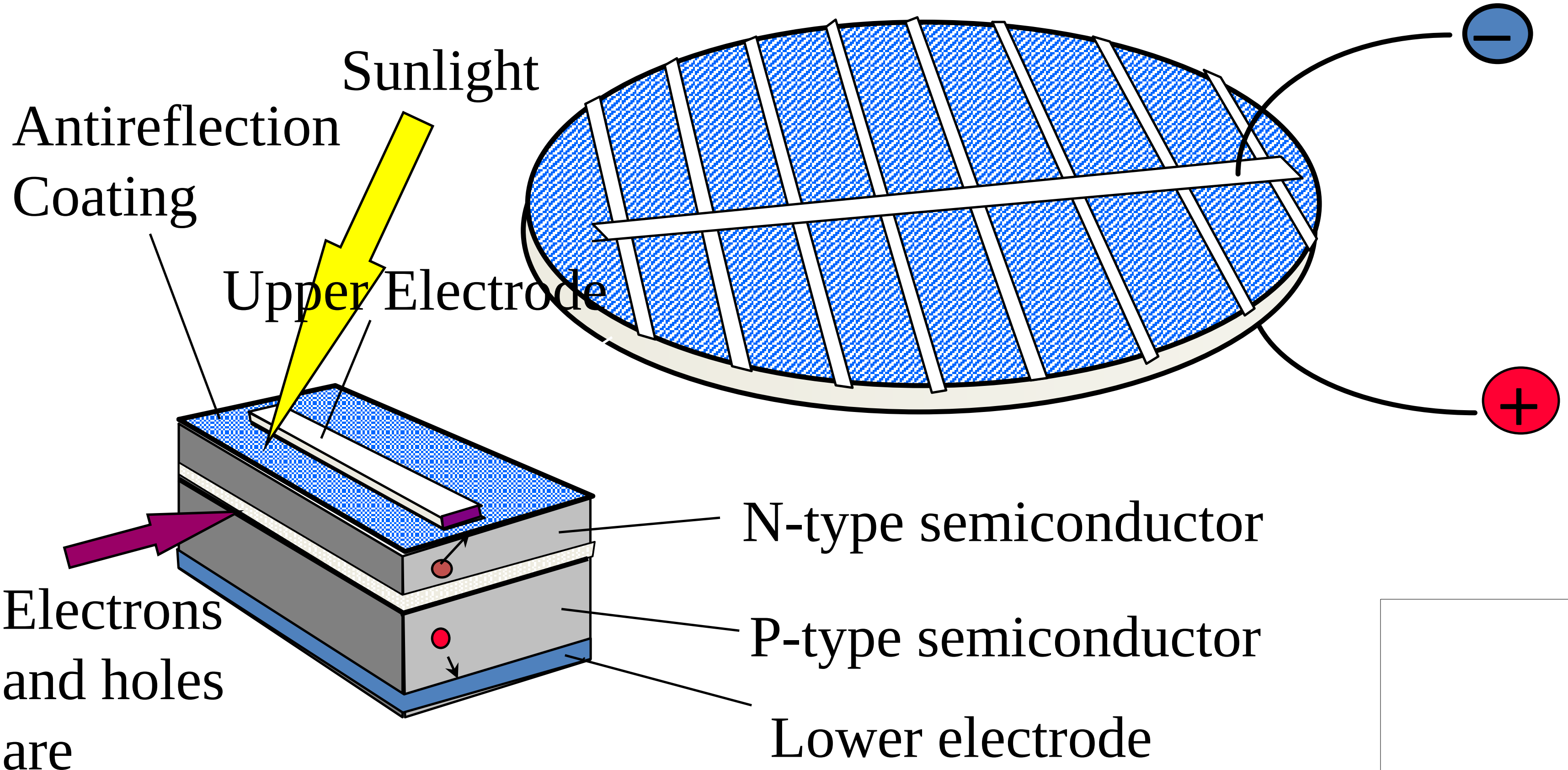
Schematic illustartion of Solar Cells



Sunlight

Antireflection Coating

Upper Electrode

N-type semiconductor

P-type semiconductor

Lower electrode

Electrons and holes are separated at the pn interface

Cell to Module

A solar panel (PV module) consists of many solar cells. Fabrication process of PV module is schematically illustrated in the right figure.

Cells are aligned on the glass panel as an array.

Solar cells requires a support since they are 0.2 to 0.3 mm in thickness. Glass panel is conventionally used as the support. Solar cells are aligned in arrays with the top surface facing the panel surface. For this purpose, a tempered glass is used, which has been subjected to a severe test, such as drop test of metal balls. Also the panel should be strong to permit workers walk on it to setup.

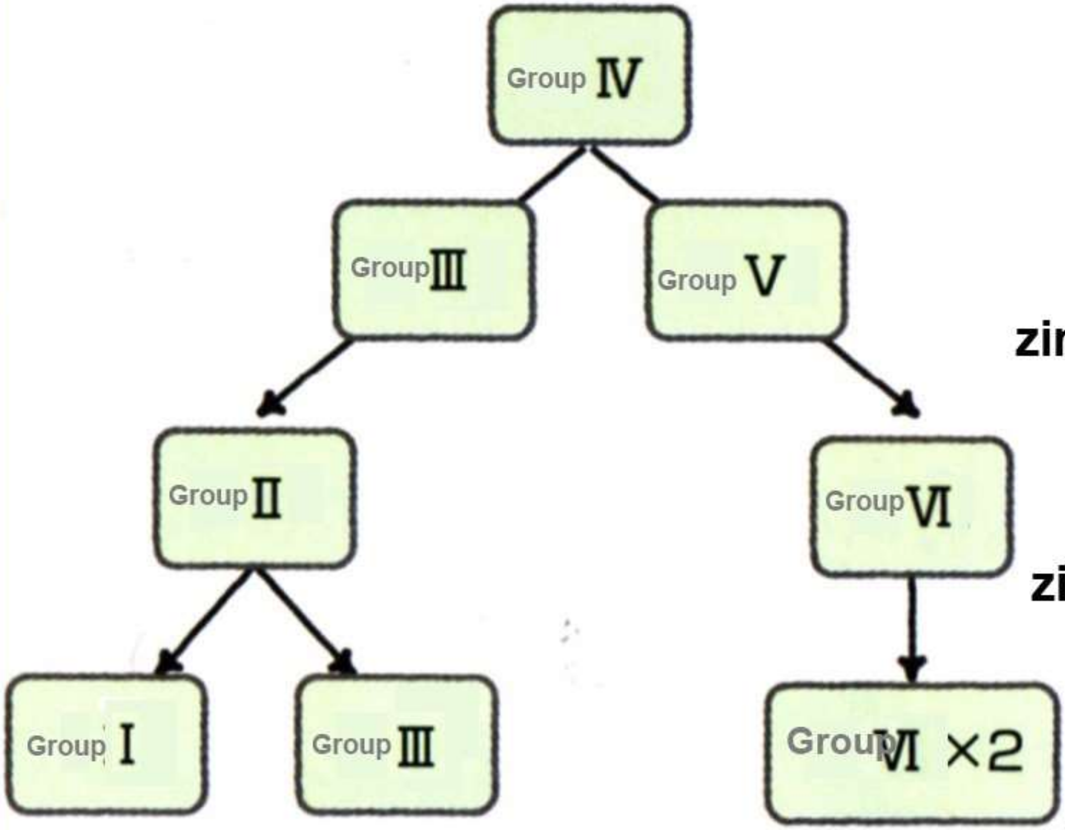
Seal with a resin and a protection film

The panel with solar cells array is sealed with a resin and a protection film. Despite the long lifetime of the solar cells, the lifetime of the PV module is rather short since it is determined by the deterioration of resin to seal.

Finally the panel is fixed to a frame and wired.

HIGH POTENTIAL OF COMPOUND SEMICONDUCTOR SOLAR CELLS

Genealogical Tree of Compound Semiconductors

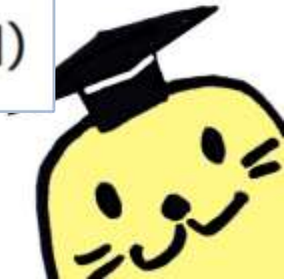


ex. Silicon (Si)
diamond structure

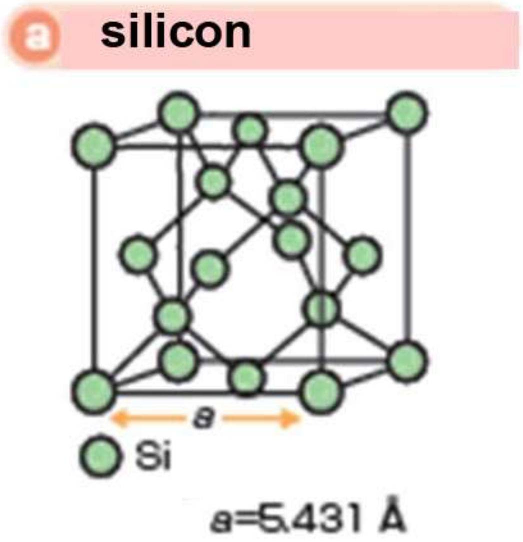
ex. Gallium Arsenide (GaAs)
zincblende structure (ZB)

ex. Cadmium Teluride (CdTe)
zincblende structure(ZB)

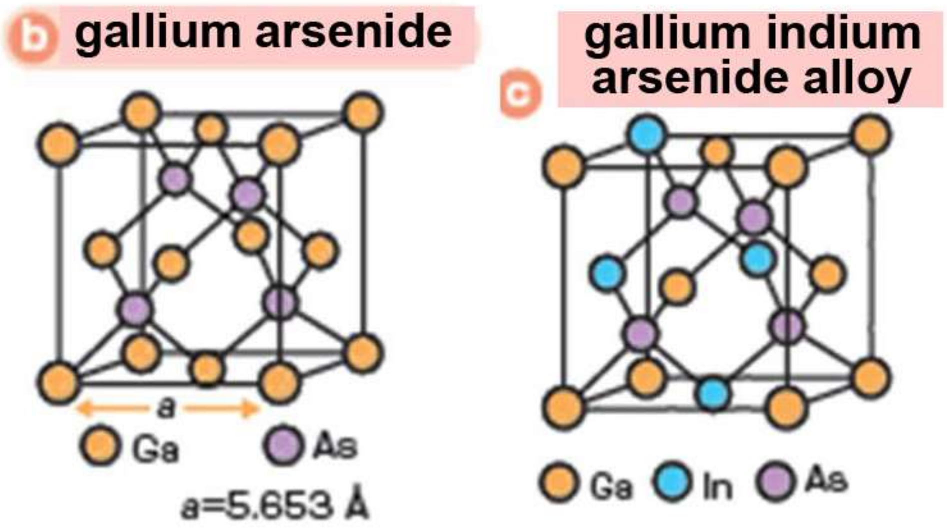
ex. Copper Indium Selenide ($CuInSe_2$)
chalcopyrite structure (CH)



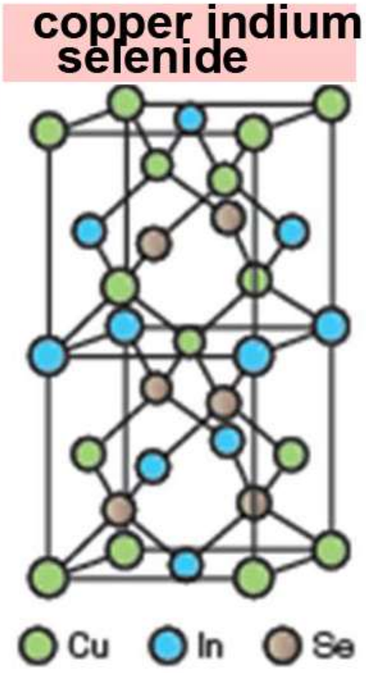
Crystal Structure of Semiconductors



diamond structure

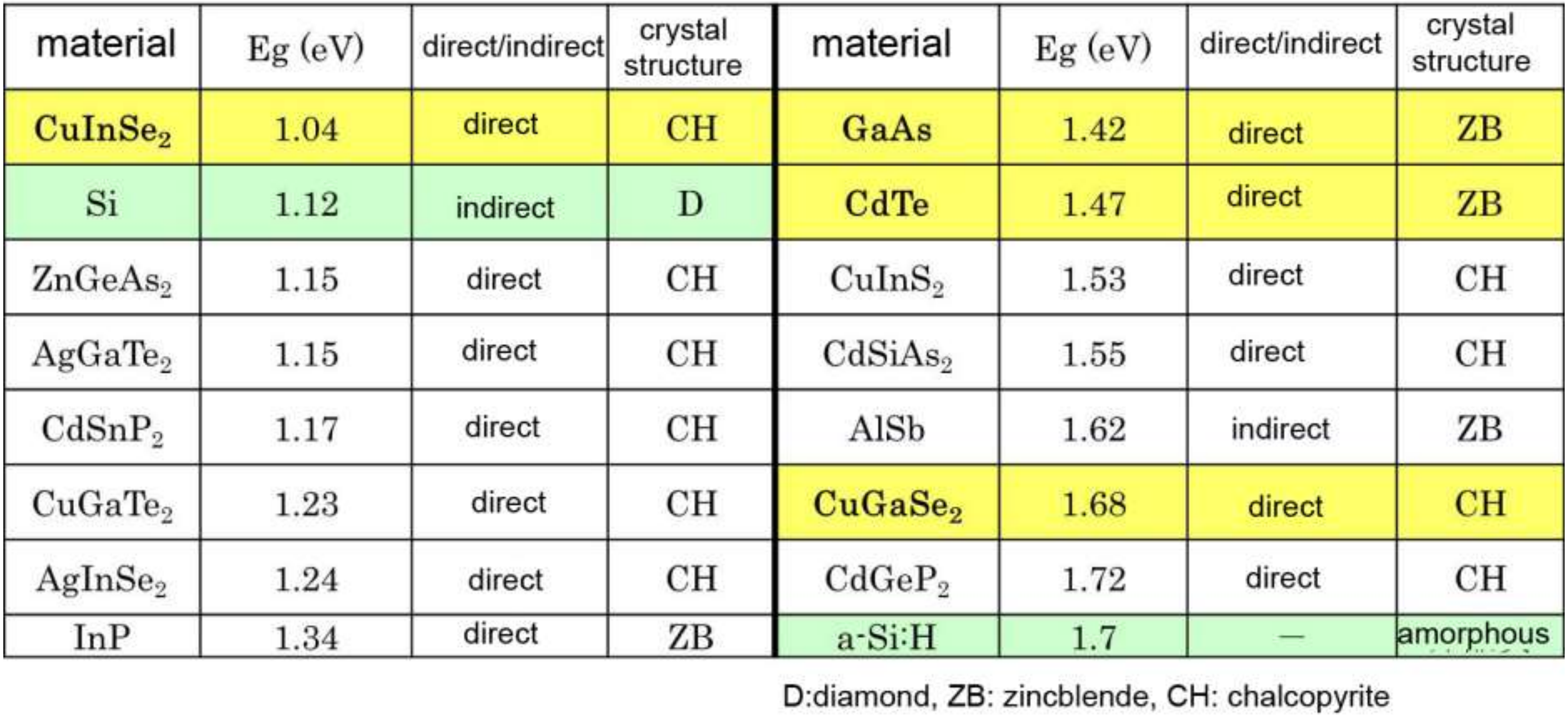


zincblende structure



chalcopyrite structure

Semiconductors with energy gap between 1.0 and 1.7 eV

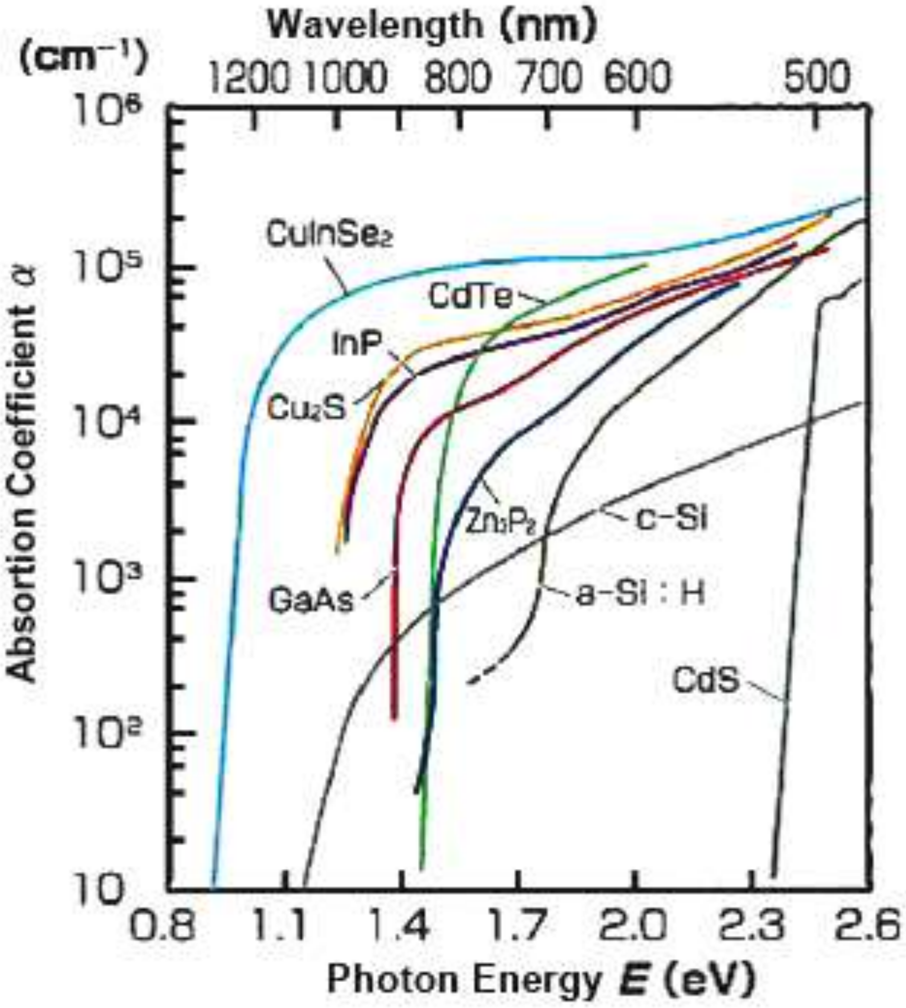


material	Eg (eV)	direct/indirect	crystal structure	material	Eg (eV)	direct/indirect	crystal structure
$CuInSe_2$	1.04	direct	CH	GaAs	1.42	direct	ZB
Si	1.12	indirect	D	CdTe	1.47	direct	ZB
$ZnGeAs_2$	1.15	direct	CH	$CuInS_2$	1.53	direct	CH
$AgGaTe_2$	1.15	direct	CH	$CdSiAs_2$	1.55	direct	CH
$CdSnP_2$	1.17	direct	CH	AlSb	1.62	indirect	ZB
$CuGaTe_2$	1.23	direct	CH	$CuGaSe_2$	1.68	direct	CH
$AgInSe_2$	1.24	direct	CH	$CdGeP_2$	1.72	direct	CH
InP	1.34	direct	ZB	a-Si:H	1.7	—	amorphous

D:diamond, ZB: zincblende, CH: chalcopyrite

Comparison of Absorption Spectra of Semiconductors

Optical absorption coefficient of crystalline silicon (c–Si) is relatively low, since silicon has a indirect energy gap. On the contrary, direct gap semiconductors, such as GaAs, CdTe, and CIS($CuInSe_2$) show two order of magnitude larger absorption coefficient compared with Si. In particular, CIS has a strong absorption in infrared region.



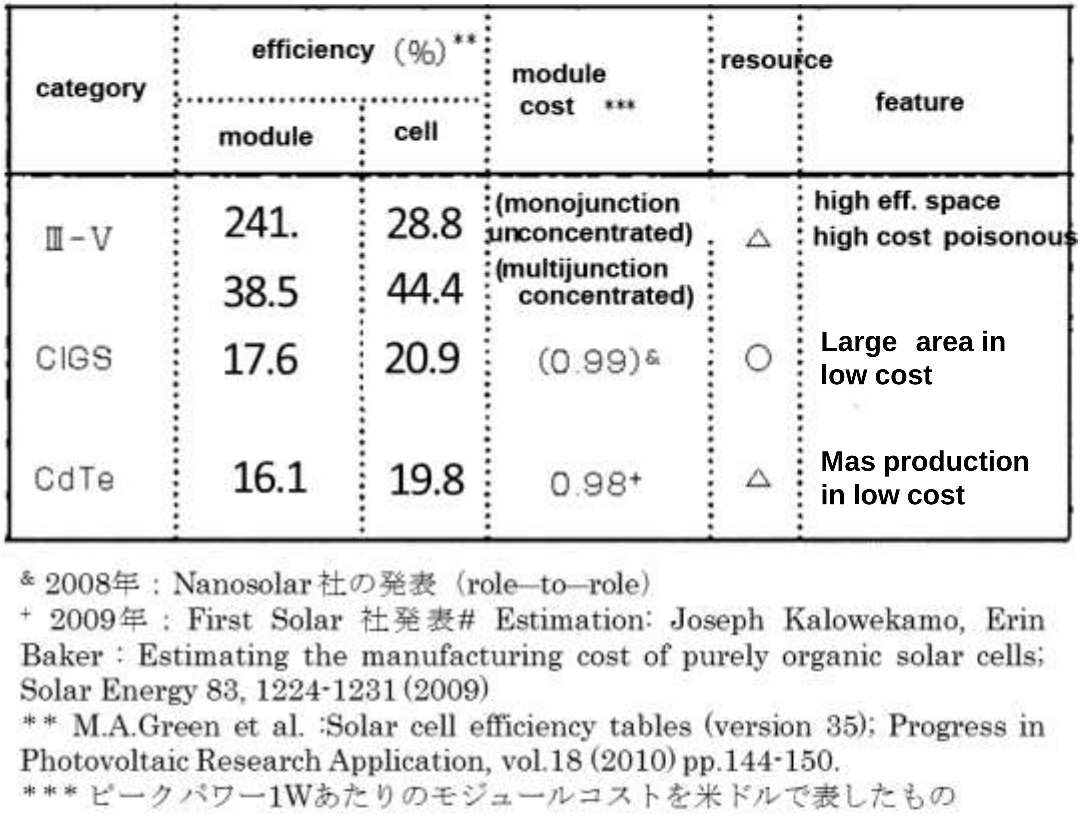
Performance of Compound Solar Cells

Comparison of three kinds of compound semiconductor cells.

Efficiency of module is very small compared with that of cell.

Crystal engineering approach may be effective to solve the problem.

Table of comparison of three types of compound solar cells



category	efficiency (%)**		module cost ***	resource	feature
	module	cell			
Ⅲ-V	241.	28.8	(monojunction unconcentrated)	△	high eff. space high cost poisonous
	38.5	44.4	(multijunction concentrated)		
CIGS	17.6	20.9	(0.99)&	○	Large area in low cost
CdTe	16.1	19.8	0.98+	△	Mas production in low cost

& 2008年：Nanosolar社の発表（role—to—role）

+ 2009年：First Solar 社発表# Estimation: Joseph Kalowekamo, Erin Baker : Estimating the manufacturing cost of purely organic solar cells; Solar Energy 83, 1224-1231 (2009)

** M.A.Green et al. :Solar cell efficiency tables (version 35); Progress in Photovoltaic Research Application, vol.18 (2010) pp.144-150.

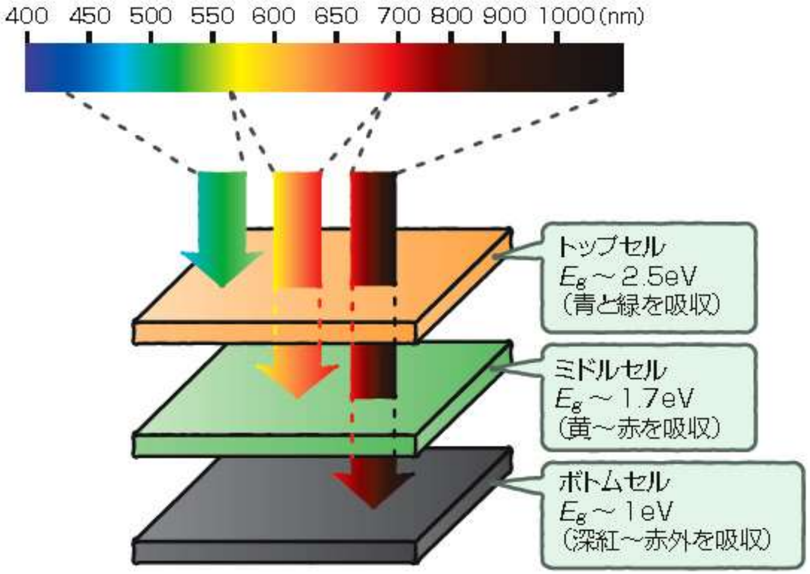
*** ピークパワー1Wあたりのモジュールコストを米ドルで表したもの

Solar Cells for Cosmic Space

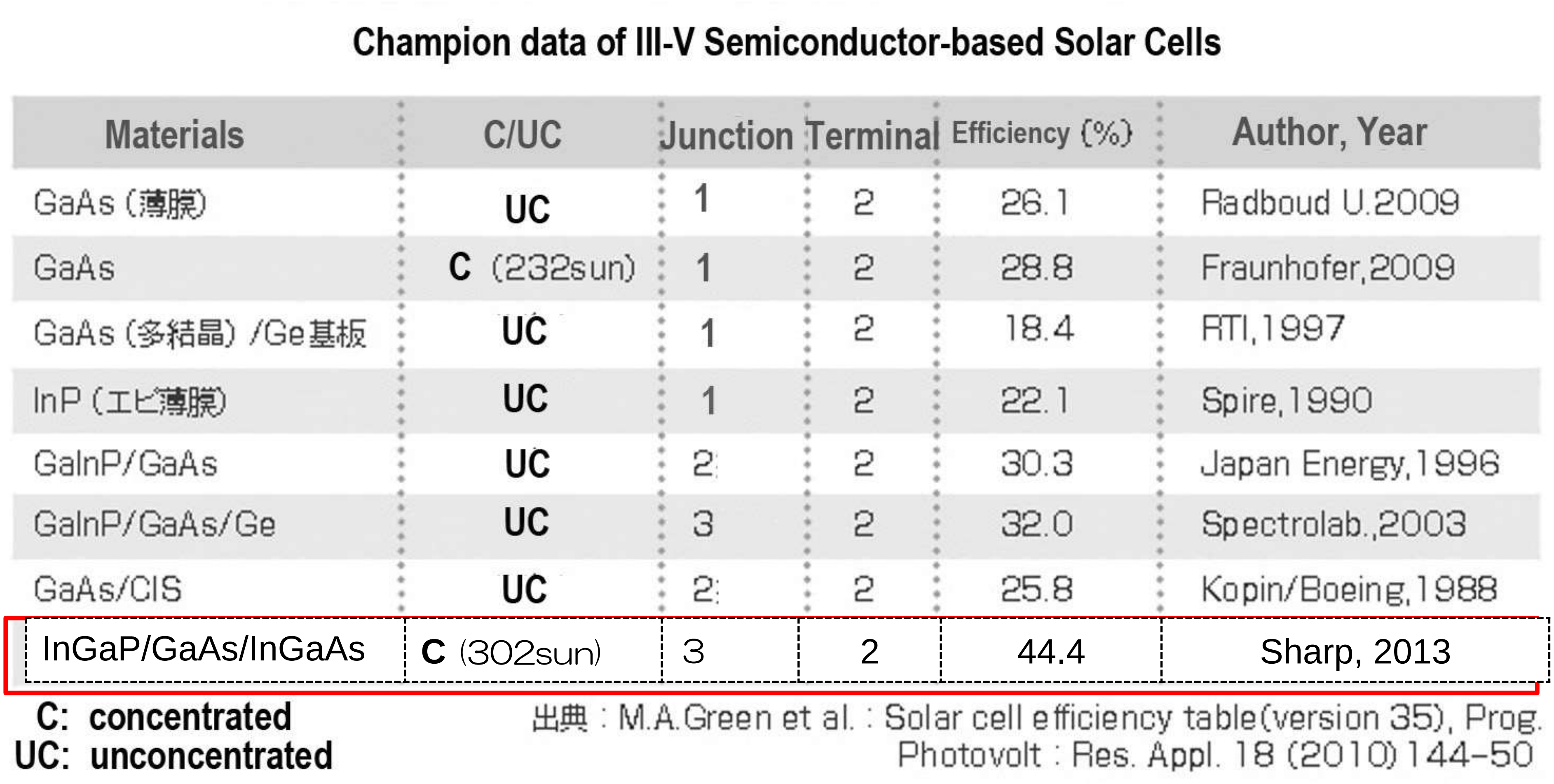
Electric power of Space Station and Artificial Satellites is supplied by High Efficiency Solar Cells.

Conversion efficiency above 40% is obtained by using a three-junction tandem structure, in which each junction takes part in a photo-electric conversion for each wavelength region as shown in the figure.

Such cell is expensive because of sophisticated process for production.



III-V Semiconductor-based Solar Cells



Champion data of III-V Semiconductor-based Solar Cells

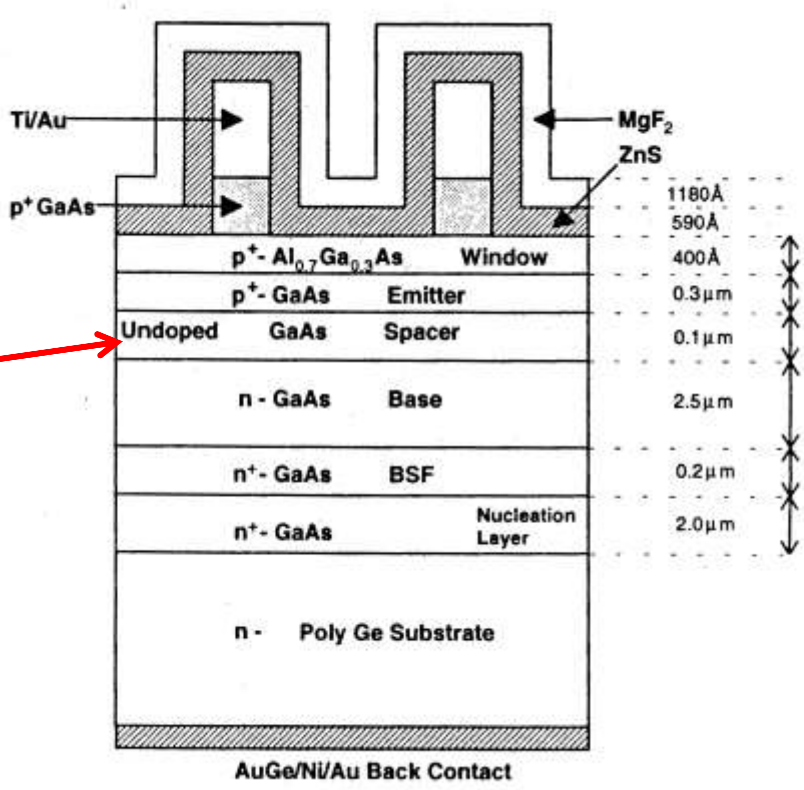
Materials	C/UC	Junction	Terminal	Efficiency (%)	Author, Year
GaAs (薄膜)	**UC**	1	2	26.1	Radboud U.2009
GaAs	**C** (232sun)	1	2	28.8	Fraunhofer,2009
GaAs (多結晶) /Ge基板	**UC**	1	2	18.4	RTI,1997
InP (エピ薄膜)	**UC**	1	2	22.1	Spire,1990
GaInP/GaAs	**UC**	2	2	30.3	Japan Energy,1996
GaInP/GaAs/Ge	**UC**	3	2	32.0	Spectrolab.,2003
GaAs/CIS	**UC**	2	2	25.8	Kopin/Boeing,1988
InGaP/GaAs/InGaAs	**C** (302sun)	3	2	44.4	Sharp, 2013

C: concentrated
UC: unconcentrated

出典：M.A.Green et al.：Solar cell efficiency table(version 35), Prog. Photovolt：Res. Appl. 18 (2010) 144–50

III-V Multicrystalline Solar Cell Thin Film Production system

- GaAs is deposited using MOCVD on an optical grade Ge polycrystalline substrate with large grains
- The structure consists of a n$^+$-nucleation layer having high concentration of As on the substrate, followed by sequenctial deposition of a thin n$^+$-BSF layer, a thick n-type base layer, a thin undoped spacer layer, a p$^+$AlGaAs window layer, finally, an n$^+$-ohmic contact layer.
- Open circuit voltage takes a large value when the spacer layer is thin.

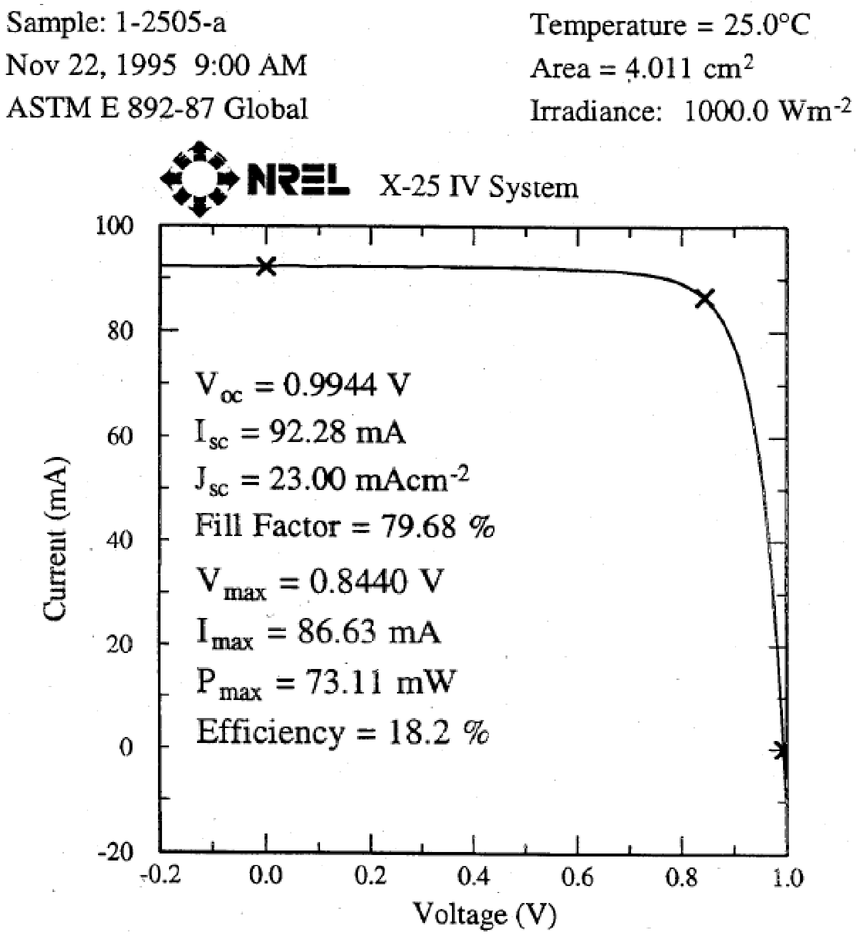


Polycrystalline P$^+$/n junction GaAs solar cells fabricated on polycrystalline Ge substrate.

R. Venkatasubramanian, B.C. O'Quinn, E. Siivola, B. Keyes, R. Ahrenkiel: Conf. Rec. 26th IEEE Photovoltaic Specialists Conf. pp.811-814 (1997)

I-V Characteristics of Multicrystaline GaAs Cell

20% efficiency for 4cm^{2}cell and 21.2% efficiency for 0.25cm^{2}cell are reported in multicrystalline GaAs cell fabricated on polycrystalline Ge substrates with sub-mm grains. Venkatasubramanian,et al.:Proc･26thIEEE Photo-voltaic Specialists Conf.(IEEE,New York,1998)



Sample: 1-2505-a
Nov 22, 1995 9:00 AM
ASTM E 892-87 Global

Temperature = 25.0°C
Area = 4.011 cm^2
Irradiance: 1000.0 Wm^{-2}

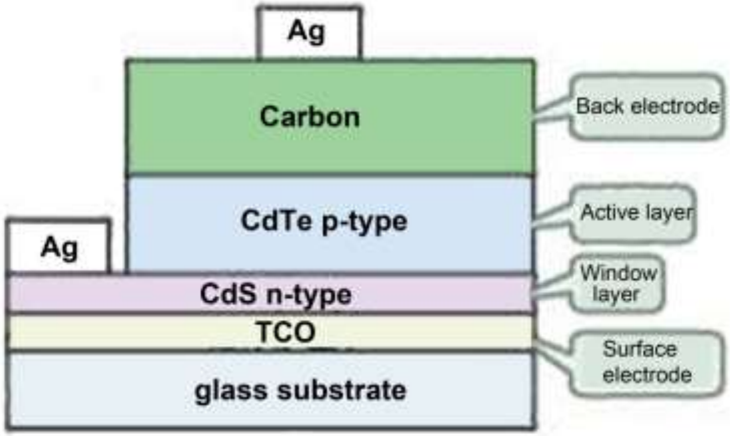
V_{oc} = 0.9944 V
I_{sc} = 92.28 mA
J_{sc} = 23.00 mAcm^{-2}
Fill Factor = 79.68 %
V_{max} = 0.8440 V
I_{max} = 86.63 mA
P_{max} = 73.11 mW
Efficiency = 18.2 %

サブmmの粒径を有する多結晶Ge基板上の多結晶GaAs太陽電池のI-V特性

Fabrication process of CdTe solar cells

The figure shows a schematic illustration of CdS/CdTe solar cells.

As shown the figure, the cell is of superstrate type; on the TCO-coated glass substrate CdS window layer is deposited, on which CdTe thin films are deposited by the close-spacing sublimation method, and covered by carbon electrode. The process is simple and suited for mass-production.



Another technique :

Glass substrate on which CdTe paste is applied and dried and CdS-coated glass substrate are confronted and heat-treated.

What is CIGS ?

CIGS is captal letter abbreviation of $CuIn_{1-x}Ga_xSe_2$.

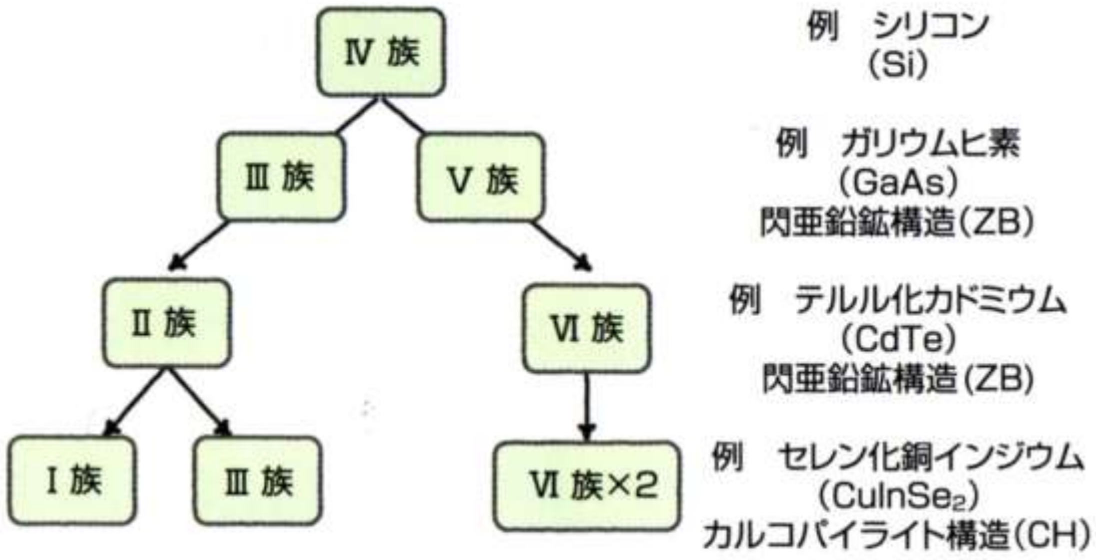
- $CuIn_{1-x}Ga_xS_2$ can be written also as CIGS, but CIGS cells in the market is only $CuIn_{1-x}Ga_xSe_2$.
- Absorption coefficient just above the energy gap of $CuInSe_2$ (=1.04eV) is said to be the larget in all known semiconductors.
- Increase Voc by alloying with $CuGaSe_2$(Eg=1.53eV).
- Highest value of conversion efficiency reported for CIGS is about 20%.
- Low materials cost and easy for manufacturing.

About CIGS

CIGS is $CuIn_{1-x}Ga_xSe_2$ which is an alloy of CIS($CuInSe_2$) and CGS($CuGaSe_2$).

CIS is a descendant of diamond family as shown by a family tree IV→III-V→II-VI→I-III-VI$_2$, a tetrahedrally coordinated covalent semiconductor.

Many candidate for solar cells are found in I-III-VI$_2$ ternary semiconductor family.



化合物	バンドギャップ(eV)	格子定数(Å)		化合物	バンドギャップ(eV)	格子定数(Å)	
		a	c			a	c
$CuInSe_2$	1.04	5.79	11.60	$CuInS_2$	1.53	5.52	11.08
$CuGaSe_2$	1.6	5.61	11.01	$CuGaS_2$	2.5	5.35	10.48
$CuAlSe_2$	2.7	5.60	10.91	$CuAlS_2$	3.5	5.32	10.43
$AgInSe_2$	1.04	6.10	11.68	$AgInS_2$	1.9	5.82	11.18
$AgGaSe_2$	1.9	5.82	11.18	$AgGaS_2$	2.7	5.75	10.29
$AgAlSe_2$	2.55	5.96	10.74	$AgAlS_2$	3.13	5.70	10.26

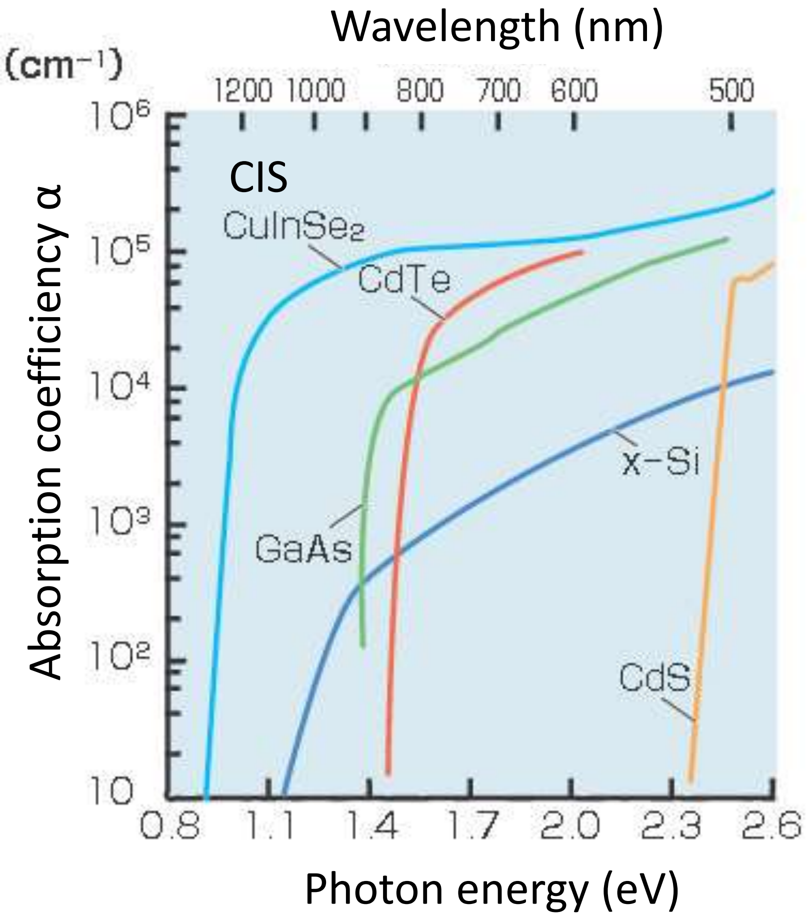
Ⅵ族がテルルのものは省略

Optical Absorption of CIGS, compared with Si

Optical absorption of Si is weak since Si has indirect absorption edge.

On the contrary, optical absorption is strong, since CIGS, CdTe, GaAs have direct gap.

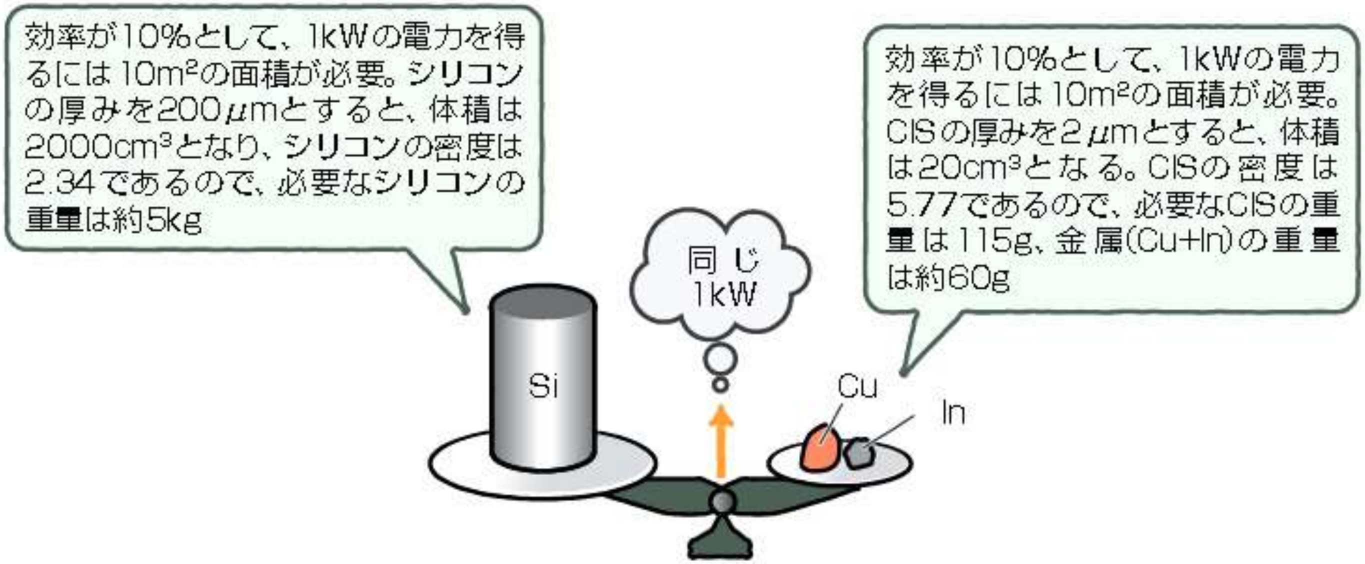
CIS absorbs near infrared wavelength and PV output is strong in the morning and evening.



Weight of silicon and Cu+In necessary to generate 1 kW

To generate 1kW, 5kg of Si is necessary while 60g Cu+In is sufficient.

This difference is due to difference in absorption coefficinent

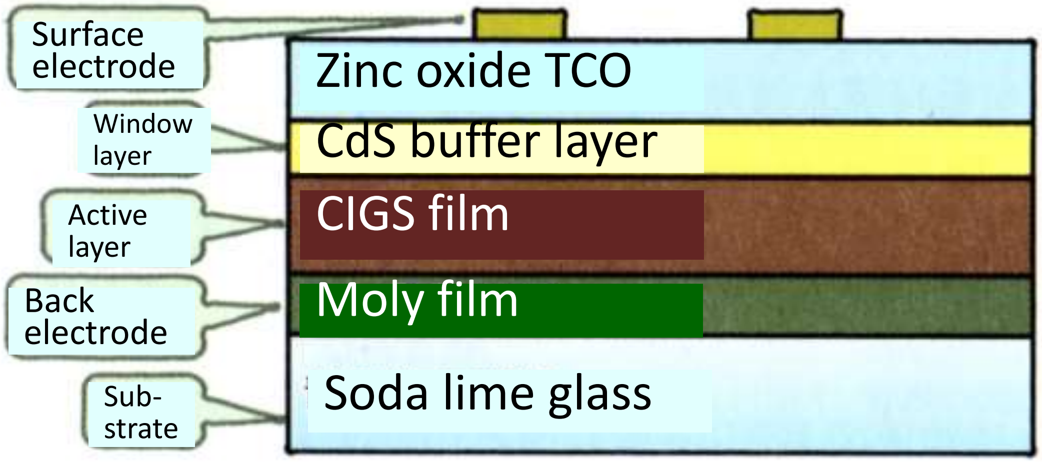


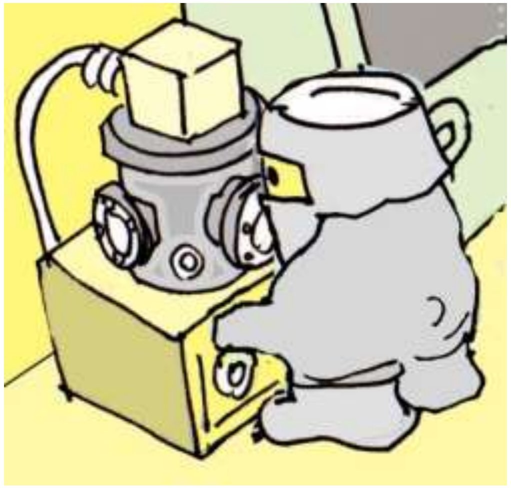
効率が10%として、1kWの電力を得るには10m^{2}の面積が必要。シリコンの厚みを200μmとすると、体積は2000cm^{3}となり、シリコンの密度は2.34であるので、必要なシリコンの重量は約5kg

効率が10%として、1kWの電力を得るには10m^{2}の面積が必要。CISの厚みを2μmとすると、体積は20cm^{3}となる。CISの密度は5.77であるので、必要なCISの重量は115g、金属(Cu+In)の重量は約60g

Fabrication Process of CIGS Film

- Since CIS（$CuInS_2$） has a direct band gap, an absorption coefficient just above the gap is so strong that films of only 1～2μm in thickness can absorb solar light efficiently.
- CIGS ($CuIn_{1-x}Ga_xS_2$) is an alloy semiconductor of CuInSe2 and CuGaSe2, with x being nearly equal to 0.25, shows an energy gap around 1.25eV, with a conversion efficiency as high as 20％ (small cell).
- Conversion efficiency of 17% comparable to Si multicrystalline module , has been demonstrated even in a large area module.



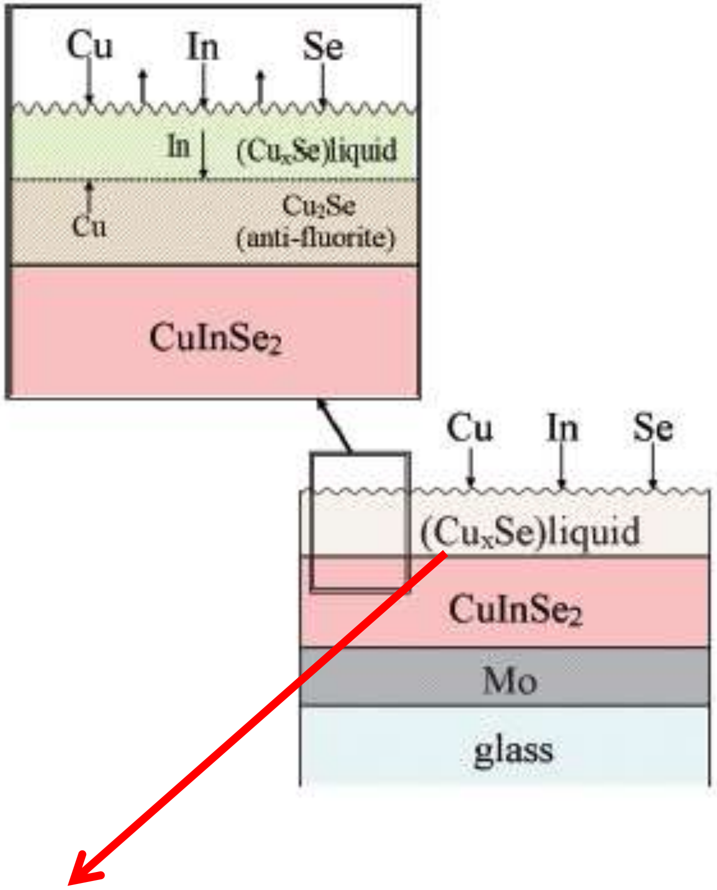


Process for CIGS cells
(1) Bilayer method

CIS crystals are formed by a solution growth through liquid phase of Cu-Se surrounding CIS grains.

Coexistence of Cu-Se liquid phase and solid phase Cu_2Se helps a reaction of the Cu_2Se and In+Se to form chalcopyrite phase CIS.

Three dimensional orientatational relation exists between Cu_2Se and CIS, which is called “topotactic” reaction.



CuxSe is removed by KCN treatments

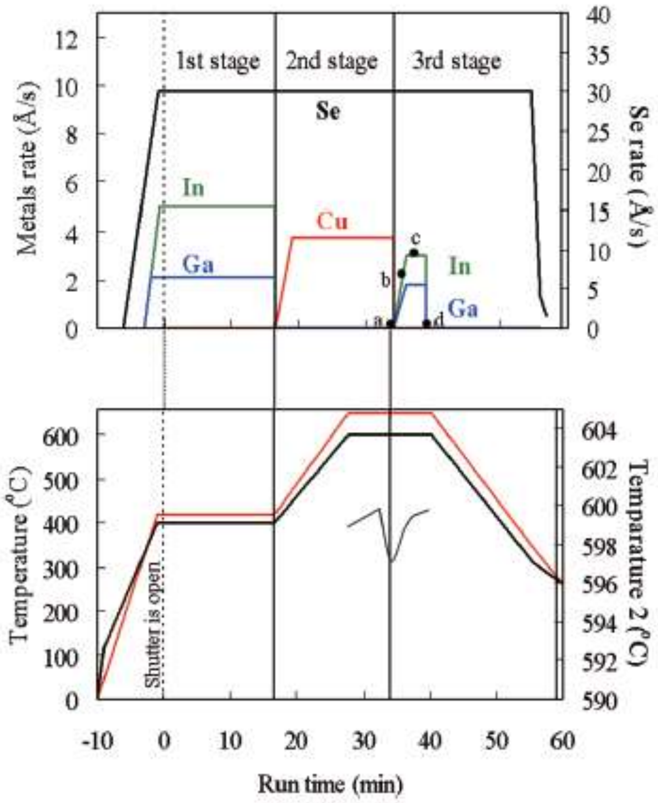
Wada ：Bul. JACG Vol. 36, No. 4（2009）282

Process for CIGS cells
(2) Three stage method

1st stage: Deposition of $(\mathrm{In,Ga})_2\mathrm{Se}_3$ films at low substrate temperature of 400 degree by co-evaporation of In, Ga and Se.

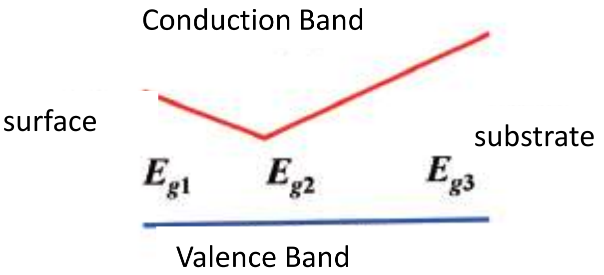
2nd stage: Deposition of Cu and Se at elevated substrate temperature of 600 degree C to form Cu-rich composition（Cu/（In+Ga）> 1）.

3rd stage: Additional evaporation of In, Ga and Se to adjust the film composition to Cu-deficient（Cu/（In+Ga）< 1）.

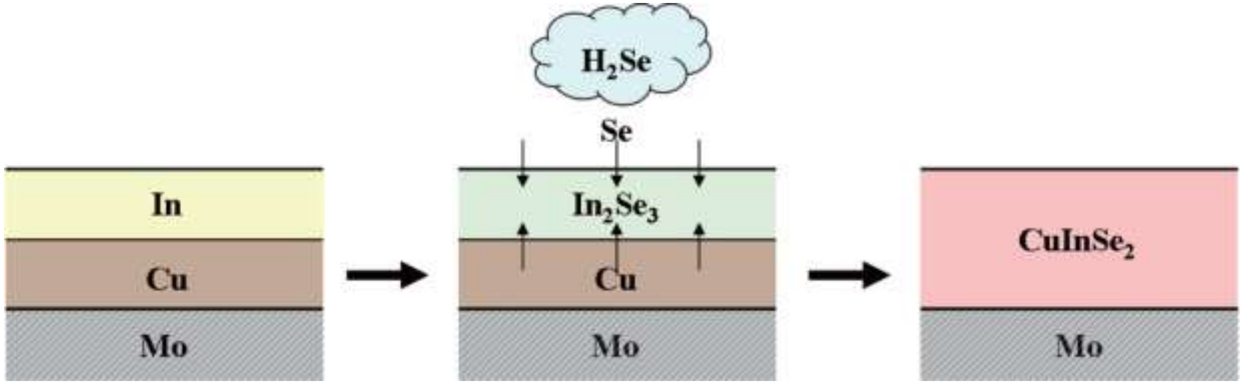


A double-graded band gap is formed by three-stage method, which inceases both Vocand Jsc

Wada: J.Jpn. Association of Crystal Growth
Vol. 36, No. 4（2009）282

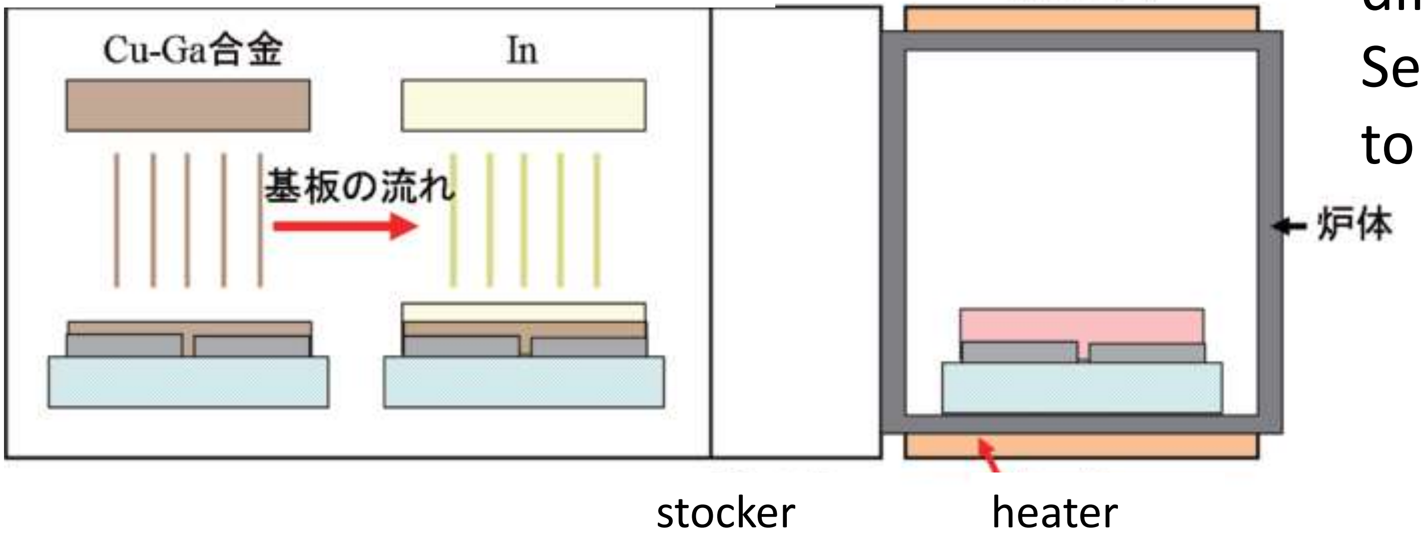


Process for CIGS cells (3) Selenization method



Metallic precursor formation process by sputtering

Selenization/sulfurization process



Sequential formation of Cu, In metallic films on Mo back electrode.

The film stack is heat-treated in a H_2Se gas atmosphere to form In_2Se_3 by reaction of In and H_2Se, followed by Cu-diffusion from back and Se-diffusion from surface to transform In_2Se_3 to CIS

Wada: JJACG Vol. 36, No. 4（2009）282

参考

Solar Frontier achieved 20.9% conversion efficiency in CIS

SOLAR FRONTIER
昭和シェル石油グループ

World record efficiency in thin film solar cells witnessed by Fraunhofer Institute, Germany

【2014.4.2 press release】-

Solar Frontier through joint research with NEDO achieved world record of conversion efficiency (20.9 %) in CIGS thin film solar cell (0.5cm^2). The value was disclosed by a German Testig Organization, Fraunhofer Institute.

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reference

World record of sub-module efficiency of 17.8% in CIGS-based solar cells.

SOLAR FRONTIER
昭和シェル石油グループ

Solar Frontier has attained 17.8% efficiency in CIGS sub-modules with 30cmx30 cm area.

2012.2.28 press release

Junction of CIS solar cell

In CIS-based solar cells a heterojunction consisting of p-$CuInSe_2$ and CBD（chemical bath deposition）n-CdS or n-ZnS ec.

Group-III element is diffused into CIS , when n-CdS is deposited by CBD to form a buried junction in $CuInSe_2$.

The fact that single crystalline CIS cell shows only a poor conversion efficiency may be explained by absence of buried junction in the epitaxilal deposition of Cd on CIS crystal.

Band discontinuity at the CdS/CIGS interface is 0.2-0.3eV for Ga composition of 25%, while it is zero for Ga composition of 40-50% and it takes a negative value above the concentration.

Research Subjects for CIGS-based Solar cells

Highest efficiency of CIGS solar cell is obtained in an alloy with Eg of 1.1 to 1.2 eV .

According to the Theoretical Limit curve, coversion efficiency exceeding 20% is expected in CIGS film with Eg value of 1.4 eV.

However crystallinity deteriorates by an increase of Ga content over 25%, which hampers improvement of efficiency.

It is also pointed out that high efficiency is obtained only in solar cells with a graded energy gap, the fact suggesting some hidden problems.

CIGS tandem cells

Conversion efficiency over 25% is expected in a CIGS-based tandem cell with Eg=1.6-1.8eV for upper cell , and Eg=0.9-1.2eV for lower cell. However there are so many problems to be solved to realize tandem cell.

Improvement of efficiency of upper cell(>16%)

Higher transparency of upper cell

Method of upper cell deposition without damage to lower cell

Short circuit current matching

（Ceramics Soc. Jpn. Ed.「Solar cells materials」5.4）

CZTS what?

The table shows the Clark number down to 30. From this table we can have perspective that silicon will survive as important material even in the next generation.

CIGS employs not so abundant materials, In, despite Cu is in rank 25. Researchers look for alternative materials for In, and found a quaternary material Cu_2ZnSnS_4 with Sn(No.30) and Zn(No.31). CZTS is an abbreviation of Copper Zinc Tin Sulfide.

Crystal structure is Kesterite. Kesterite is an mineral with $Cu_2(Zn,Fe)SnS_4$ formula.

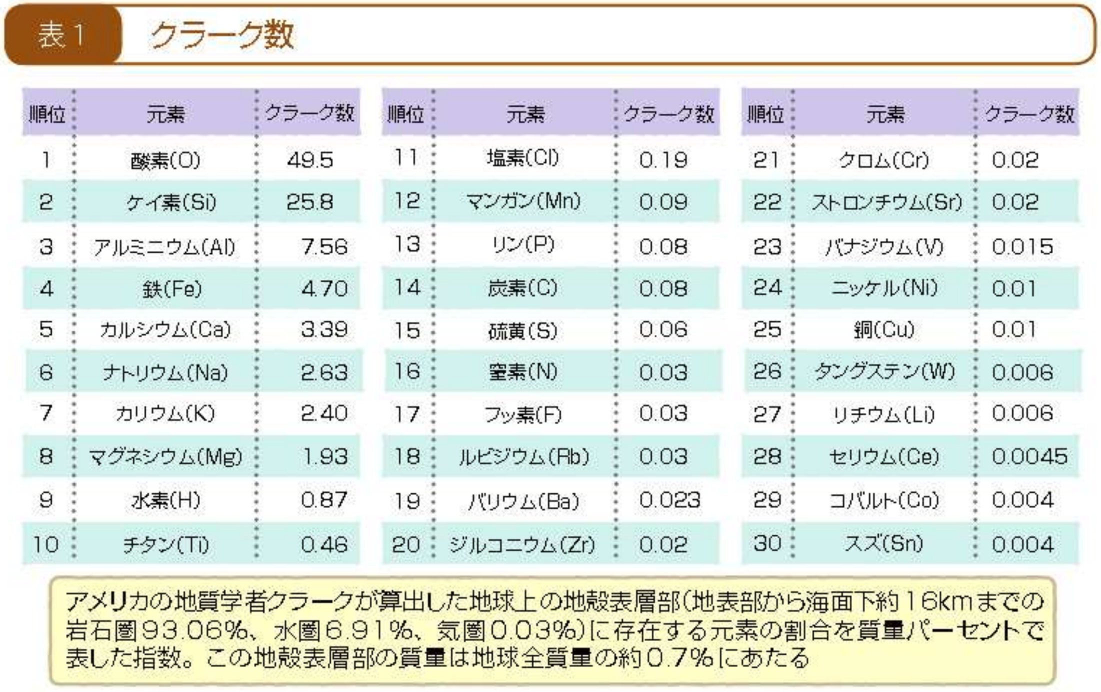
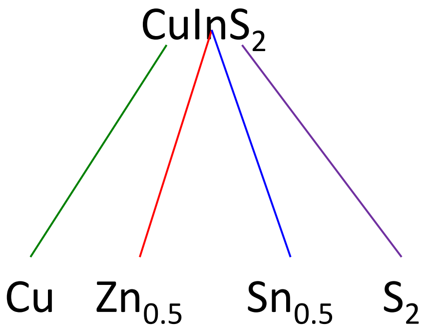


表 1 クラーク数

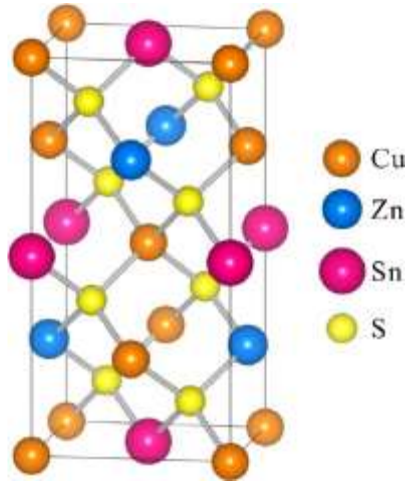
順位	元素	クラーク数	順位	元素	クラーク数	順位	元素	クラーク数
1	酸素(O)	49.5	11	塩素(Cl)	0.19	21	クロム(Cr)	0.02
2	ケイ素(Si)	25.8	12	マンガン(Mn)	0.09	22	ストロンチウム(Sr)	0.02
3	アルミニウム(Al)	7.56	13	リン(P)	0.08	23	バナジウム(V)	0.015
4	鉄(Fe)	4.70	14	炭素(C)	0.08	24	ニッケル(Ni)	0.01
5	カルシウム(Ca)	3.39	15	硫黄(S)	0.06	25	銅(Cu)	0.01
6	ナトリウム(Na)	2.63	16	窒素(N)	0.03	26	タングステン(W)	0.006
7	カリウム(K)	2.40	17	フッ素(F)	0.03	27	リチウム(Li)	0.006
8	マグネシウム(Mg)	1.93	18	ルビジウム(Rb)	0.03	28	セリウム(Ce)	0.0045
9	水素(H)	0.87	19	バリウム(Ba)	0.023	29	コバルト(Co)	0.004
10	チタン(Ti)	0.46	20	ジルコニウム(Zr)	0.02	30	スズ(Sn)	0.004

アメリカの地質学者クラークが算出した地球上の地殻表層部(地表部から海面下約16kmまでの岩石圏93.06%、水圏6.91%、気圏0.03%)に存在する元素の割合を質量パーセントで表した指数。この地殻表層部の質量は地球全質量の約0.7%にあたる



$CuInS_2$

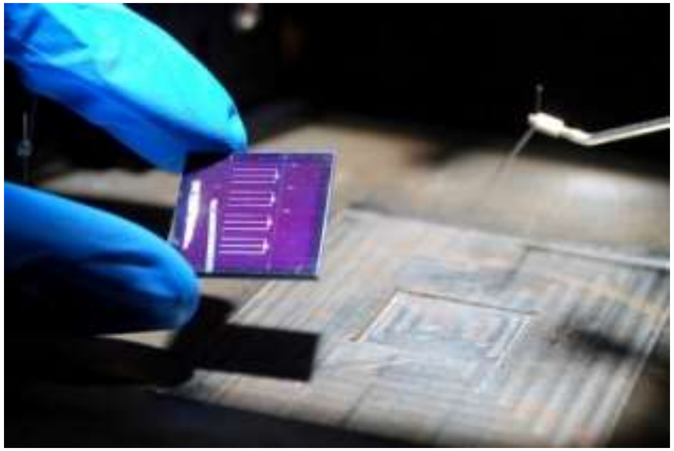
Cu $Zn_{0.5}$ $Sn_{0.5}$ S_2



World recored efficiency of 12.6% in CZTS

Solar Frontier ,, IBM corporation and Tokyo Ouka Industry jointly published a report that they obtained 12.6% efficiency in CZTS solar cell with an area of 0.42cm².

Advanced Energy Materials 1Nov. 27 , 2012



写真は
2012年8月30日
プレスリリース

写真提供：IBMコーポレーション（www.research.ibm.com）

Energy Payback Time of Solar Cells

- Energy payback time means the time necessary to recover the energy payed for production of solar cells by PV generation.
- Energy payback time is calculated from a ratio of total production energy of components consisting of the PV system to total energy produced by the system per one year.
- Production energy gradually decreases by improvement of technology and expansion of scale of production. The latter increases by improvement of conversion efficiency of solar cells, which decrease the payback time every year.

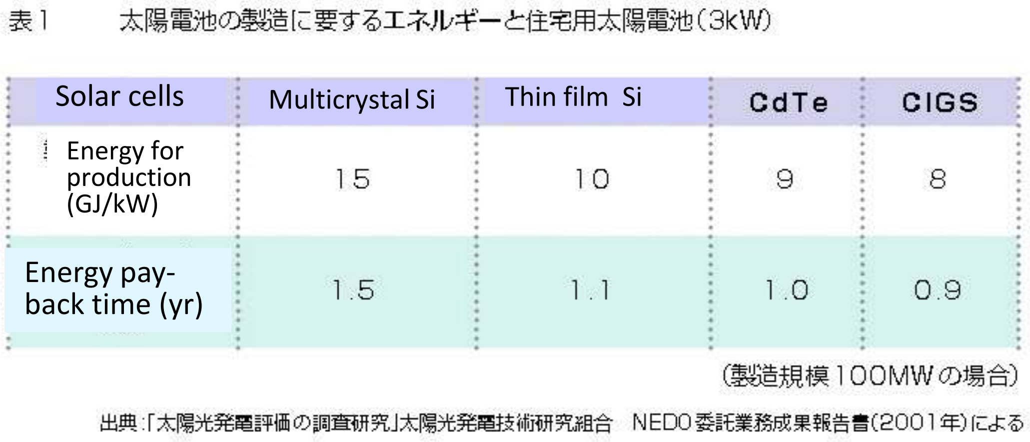


表1　太陽電池の製造に要するエネルギーと住宅用太陽電池(3kW)

Solar cells	Multicrystal Si	Thin film Si	CdTe	CIGS
Energy for production (GJ/kW)	15	10	9	8
Energy pay-back time (yr)	1.5	1.1	1.0	0.9

(製造規模100MWの場合)

出典:「太陽光発電評価の調査研究」太陽光発電技術研究組合　NEDO委託業務成果報告書(2001年)による

ORGANIC SOLAR CELLS
ORGANIC/INORGANIC HYBRID CELLS

Organic Solar Cell and Dye-Sensitized Solar Cell

Both cells utilize photo-generation of electron-hole pair in organic molecules. Resistivity of organic semiconductors are inherently high compared with that of inorganic semiconductor. N- and p-type semiconductors are realized not by doping. The material becomes n-type if it can accept electron, or becomes p-type it can donate electron, determined by relative position of work function.

電極 | DDDDD | AAAAA | 電極

↓光励起

電極 | DDDD$D^{+\cdot}$ | $A^{-\cdot}$AAAA | 電極

↓電荷輸送

電極 | $D^{+\cdot}$DDDD | AAAA$A^{-\cdot}$ | 電極

↓起電力発生

(+)電極 | DDDDD | AAAAA | 電極(-)

↓ 電流発生 ↑

D:電子供与体(p 型); A:電子受容体(n 型)

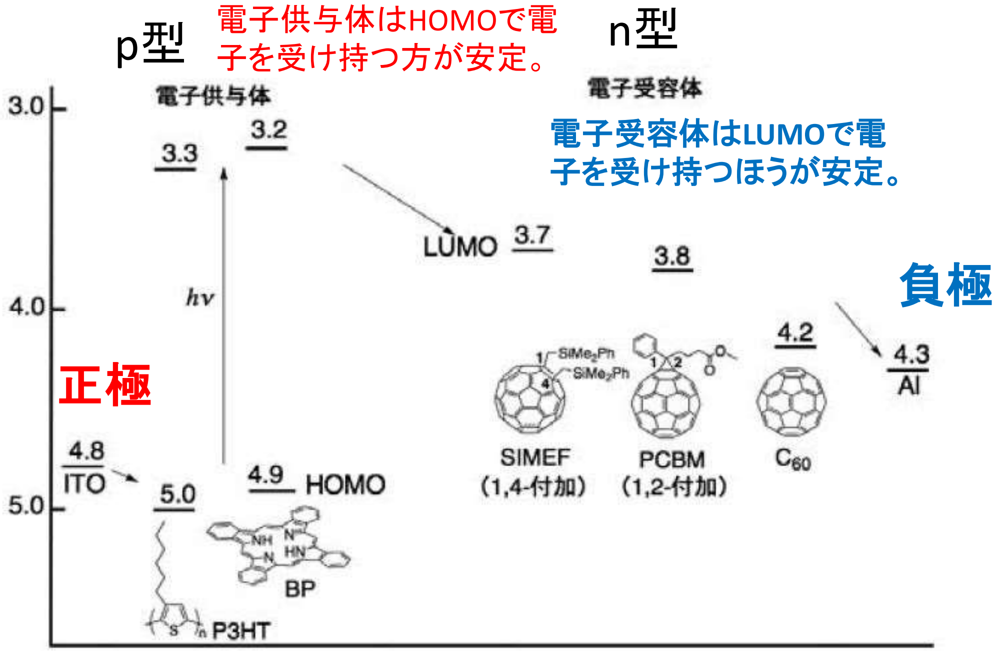
Mechanism of PV generation in organic cell

Photoexcitation of “electron donor” excites an electron from HOMO to LUMO.

Electron move from LUMO level of “donor” to the LUMO level of “acceptor” and charge separation occurs.

Here a hole is populated on the HOMO level of “donor” and an electron is populated on the LUMO level of “acceptor”.

Hole goes up along the energy diagram without barrier, and reaches to ITO electrode from “donor”.



電子供与体はHOMOで電子を受け持つ方が安定。

電子受容体はLUMOで電子を受け持つほうが安定。

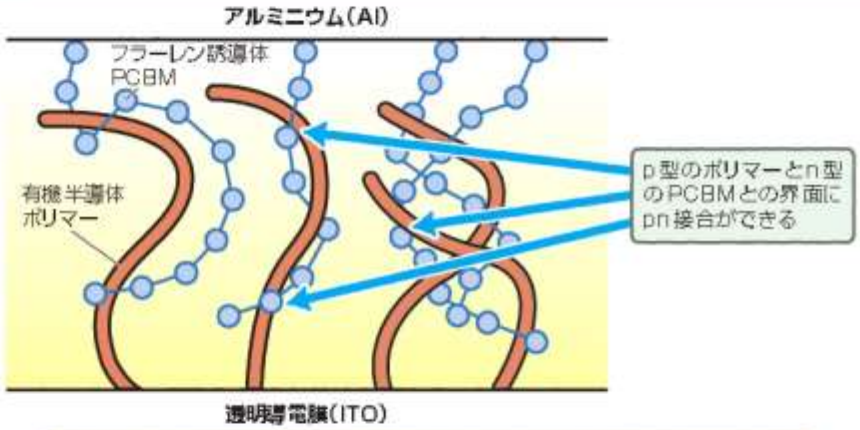
図　有機薄膜太陽電池のエネルギーダイアグラム

- While electron is captured by Al electrode with low work function from the LUMO of “acceptor”.

Bulk hetero solar cell

- This cell can be produced by painting. “Acceptors” and “donors” are entangled each other, in contrast to inorganic cells in which separation of p- and n- areas is distinct. The structure is named “Bulk Hetero” structure.
- Only the interface between two molecules are acting for photo-carrier eneration.

図1 バルクヘテロ構造有機太陽電池の内部構造の模式図



バルクヘテロ型有機太陽電池では、透明導電膜ITOをつけたガラス基板上に、電子受容体(p型)の有機半導体ポリマーと電子供与体(n型)のフラーレン誘導体PCBMとの混合物を塗布し、裏面電極としてアルミニウムをつける。光照射によって、有機半導体で光キャリアのペアが生じ、ポリマーとPCBMが絡み合って接触する界面の内蔵電位差で分離され、ITOがマイナス、アルミニウムがプラスになる

Dye-Sensitized Cell

- By light irradiation electrons on the pigment molecules are excited to LUMO level, which is slightly higher in energy than the bottom of the conduction band of TiO2. Then electrons are transferred to conduction band and flow to the outer circuit.
- On the other hand, holes left in the HOMO of molecular orbitals of pigment move to iodide ions to oxidize it. Iodines are reduced to iodide ions by getting electrons from electrode.
- Voc is the difference between Fermi level of TiO2 and REDOX of iodine.

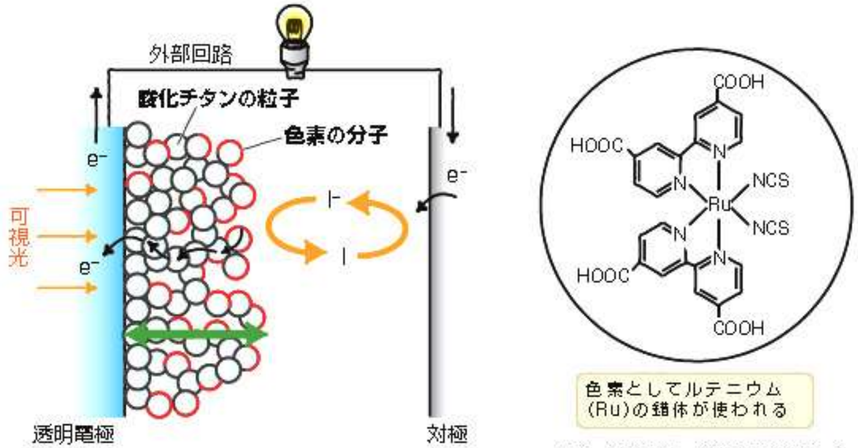


図1 色素増感太陽電池の構造と動作原理

出典：NIMS Now 8[11](2008)p6

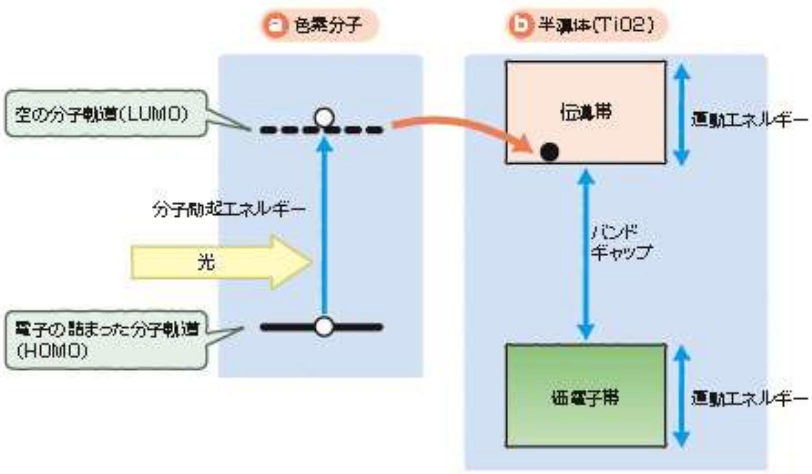
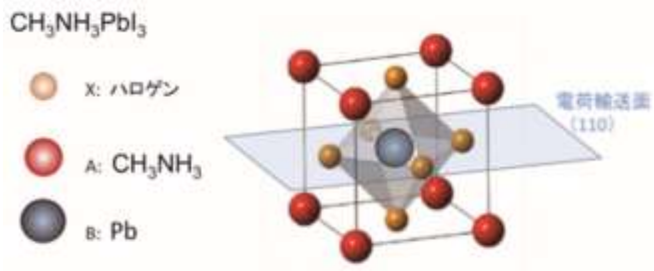


図1 分子と半導体のエネルギー準位の違い

Organic/Inorganic hybrid Perovskite Solar Cell



- Efficiency exceeding 16% (recently 20%) is obtained by using perovskite crystal of organic/inorganic hybrid.
- The perovskite has a composition $CH_3NH_3PbX_3$（X =halogen）films can be easily formed by painting and drying.
- The unique property is discovered in Japan on 1990’s. First report of PV generation is reported by Miyasaka in 2009.
- In early stage it was used as sensitizer in DSS, but in 2012 they combined it with organic hole-transporting material to get conversion efficiency higher than 10%.
- The work was selected as Breakthrough of the year in 2013 by Science journal.
- High absorption coefficient and high Voc are responsible to the hight efficiency.

Ending remarks

Future of PV generation depends on fabrication of low cost, less recourse consuming and highly efficient solar module production.

Compound semiconductors are expected as good candidate for this purpose. However, until now we have not attained efficiency of theoretical limit.

There are rooms for developing high performance cells in compound of ternary and multinary materials as well as organic/inorganic hybrid materials.

We hope challenges of young students to this area.

Appendix

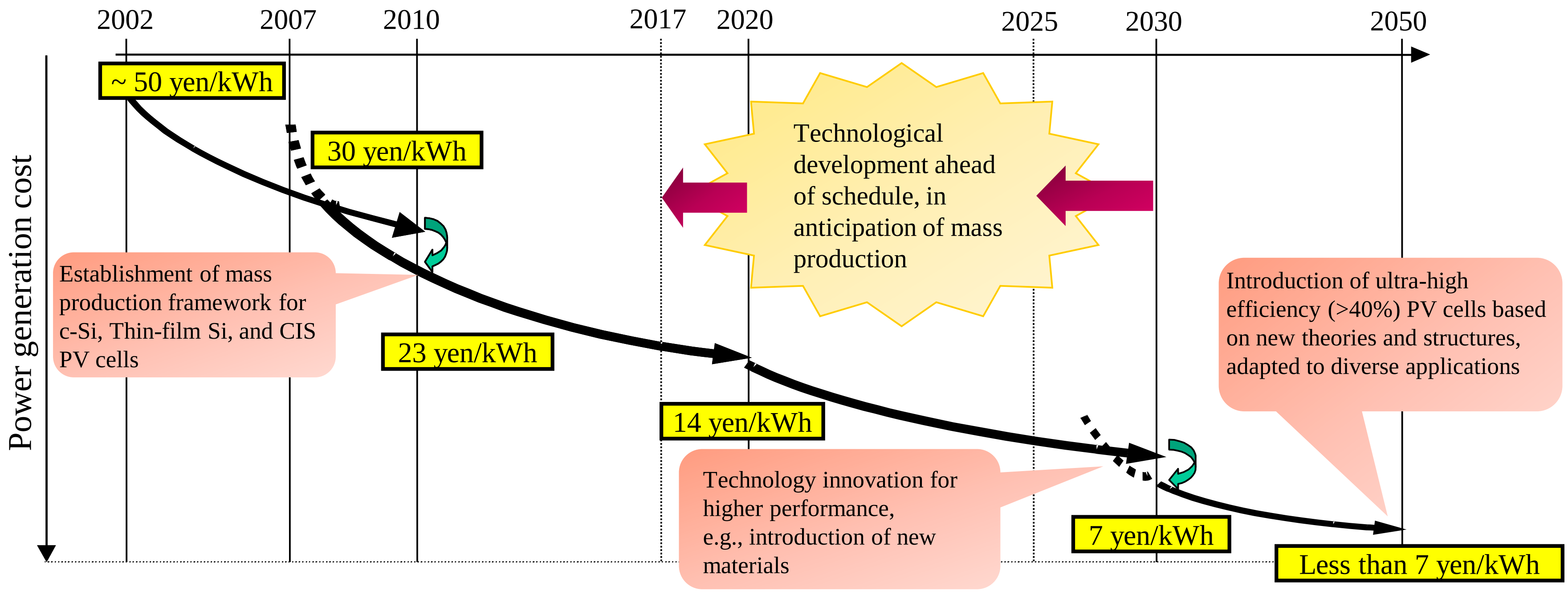
TRENDS OF PV POLICY

R&D Portfolio of NEDO for new energies

NEDO's Budget (FY2013) Total: 121.0 billion Yen (1,210 million US$)
R&D Budget for New Energy: 28.1 billion Yen (281 million US$)

Category	Classification	Budget 2013 FY
Renewable Energy	Solar Photovoltaic	9.3 billion yen (93 million US$)
	Biomass	3.6 billion yen (36 million US$)
	Wind power	5.0 billion yen (50 million US$)
	Ocean	2.5 billion yen (25 million US$)
	Geothermal	0.5 billion yen (5 million US$)
Hydrogen Tech.	Hydrogen &Fuel Cell	7.2 billion yen (72 million US$)
Total		28.1 billion yen (281 million US$)

PV R&D Roadmap in Japan (PV2030+)



Establishment of mass production framework for c-Si, Thin-film Si, and CIS PV cells

Technological development ahead of schedule, in anticipation of mass production

Technology innovation for higher performance, e.g., introduction of new materials

Introduction of ultra-high efficiency (>40%) PV cells based on new theories and structures, adapted to diverse applications

Target (completion of development)	2010 or later	2020 (2017)	2030 (2025)	2050
Power generation cost	Equivalent to household electric rates (23 yen/kWh)	Equivalent to commercial electric rates (14 yen/kWh)	Equivalent to power generation costs (7 yen/kWh)	Used as general power source (less than 7 yen/kWh)

Source: NEDO PV R&D Roadmap (PV2030+), 2009

Promotion of Green Innovation by JST's Strategic Basic Researches (1) CREST*

Category	Title	Supervisor
Energy carriers	Creation of Innovative Core Technology for Manufacture and Use of Energy Carriers from Renewable Energy Research	K. Eguchi
Phase interface science	Phase Interface Science for Highly Efficient Energy Utilization Research	N. Kasagi
Carbon dioxide utilization	Creation of essential technologies to utilize carbon dioxide as a resource through the enhancement of plant productivity and the exploitation of plant products	A. Isogai
Bioenergy Production	Creation of Basic Technology for Improved Bioenergy Production through Functional Analysis and Regulation of Algae and Other Aquatic Microorganisms	T. Matsunaga
Solar energy	Creative research for clean energy generation using solar energy	M. Yamaguchi
Water system	Innovative Technology and System for Sustainable Water Use	S. Ohgaki
Carbon dioxide emission control	Creation of Innovative Technologies to Control Carbon Dioxide Emissions	I. Yasui

CREST is a team-oriented research program aiming to generate breakthroughs with a significant impact on the development of science and technology and providing tangible benefits to society

Promotion of Green Innovation by JST's Strategic Basic Researches (2) PRESTO*

Category	Title	Supervosor
Energy carrier	Creation of Innovative Core Technology for Manufacture and Use of Energy Carriers from Renewable Energy	K. Eguchi
Phase Interface	Phase Interfaces for Highly Efficient Energy Utilization	N. Kasagi
Carbon dioxide utilization	Creation of essential technologies to utilize carbon dioxide as a resource through the enhancement of plant productivity and the exploitation of plant products	A. Isogai
Bioenergy production	Creation of Basic Technology for Improved Bioenergy Production through Functional Analysis and Regulation of Algae and Other Aquatic Microorganisms	T. Matsunaga
Solar Cells	Photoenergy conversion systems and materials for the next generation solar cells	S. Hayase
Chemical conversion	Chemical conversion of light energy	H. Inoue

*PRESTO(Precursory Research for Embryonic Science and Technology)

Promotion of Green Innovation by JST's Strategic Basic Researches (3) ALCA*

Solar Cell and Solar Energy Systems	14 projects
Superconducting Systems	8 projects
Electric Storage Devices	18 projects
Ultra Heat-Resistant Materials and High Quality Recycled Steel	13 projects
Innovative Energy-Saving and Energy-Producing Chemical Processes	13 projects
Innovative Energy-Saving and Energy-Producing Systems and Devices	7 projects
Next-generation Rechargeable Battery	4 projects
Energy Carrier	1 project

ALCA: Advanced Low Carbon Energy Research and Development Program