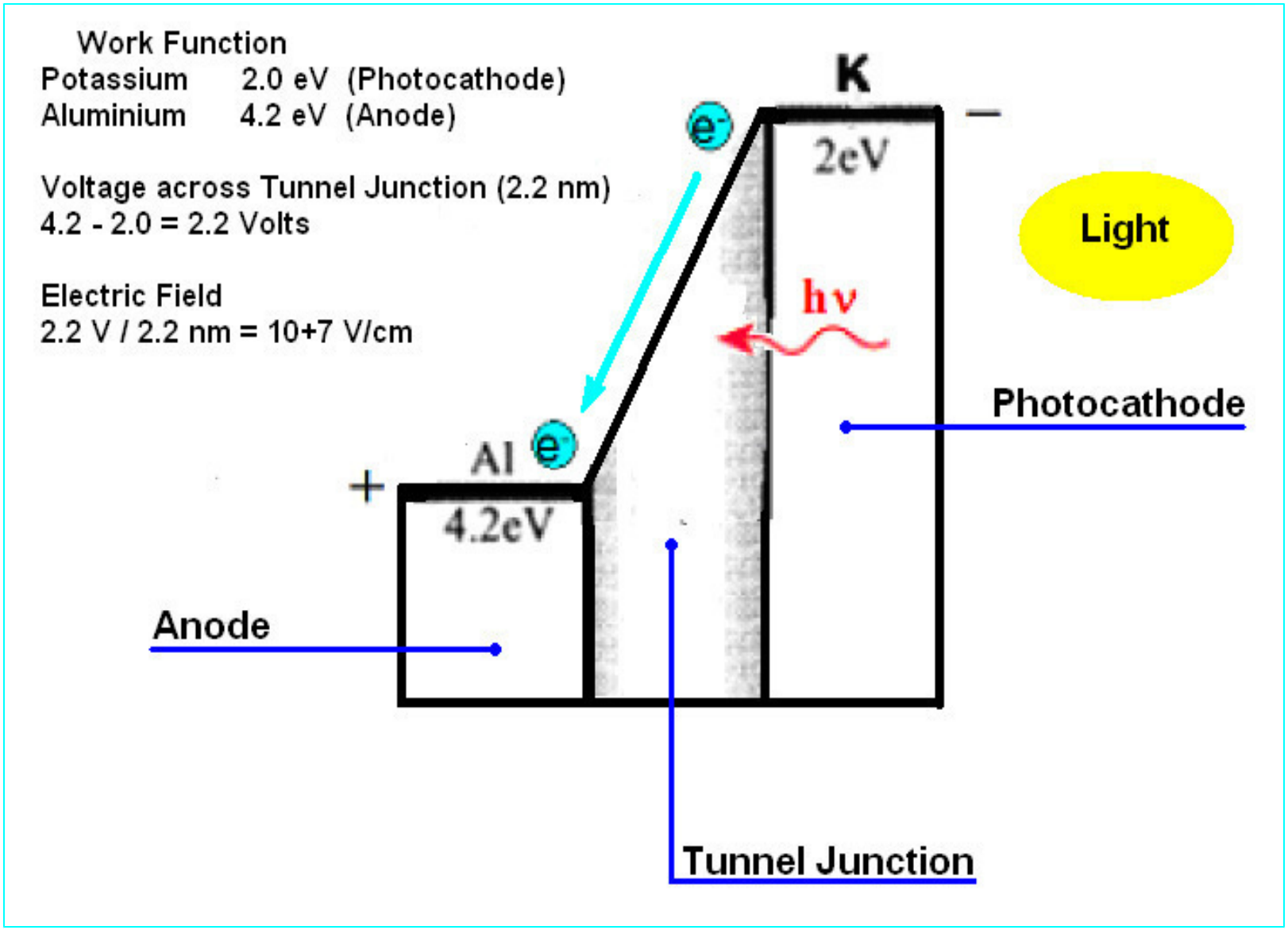
Photoinduced Electron Tranfer



Galbiati, “a thin film photovoltaic device with alkali metal active region”,
patent GB2468526A, (2010)

Arnaldo Galbiati, admin@solaris-photonics.com

A Novel Ultra Thin Film Photovoltaic Technology with Alkali Metal Active Region

Arnaldo Galbiati

Solaris Photonics, London, United Kingdom
admin@solaris-photonics.com

A Novel Ultra Thin Film Photovoltaic Technology with Alkali Metal Active Region

Outline:

- Introduction
- Photoelectric Effect: Internal & External
- Visible Light and Alkali Metals Photoionization
- Ultra Thin Film Photovoltaic Technology
- Advantages over current technology
- Efficiency
- Conclusions

Arnaldo Galbiati, admin@solaris-photonics.com

A Novel Ultra Thin Film Photovoltaic Technology with Alkali Metal Active Region

Introduction

- The aim of this paper is to present the development of novel solar cells which employ alkali metals as key photoactive material to directly convert photons of light into electricity.

- Alkali metals possess the unique property among all the other elements in the periodic table of being able to be ionized by photons of visible light, which is the reason why they are the key component in photocathode-photomultiplier technology for high efficiency light detection.

Arnaldo Galbiati, admin@solaris-photonics.com

A Novel Ultra Thin Film Photovoltaic Technology with Alkali Metal Active Region

Introduction

There has been an active search for cost effective photovoltaic devices since the development of the first Silicon solar cell in the 1950s.

- In conventional solar cells, electron-hole pairs are created by light absorption in a semiconductor, with charge separation and collection accomplished under the influence of the internal electric field of a p-n junction.
- Here we propose a novel photovoltaic device structure in which photon absorption instead occurs in an ultrathin alkali metal layer (photocathode) and where photoexcited electrons travel through a tunnel junction to reach a high work function metal layer (anode) and thus induce a photocurrent output.

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The proposed devices will make use of:

1) an ultra thin (<30 nm) highly photoemissive alkali layer (Photocathode) for electron emission under light.

2} an ultra thin layer (<5 nm) of semiconducting or insulating material (Tunnel Junction) for charge separation.

3) a metal electrode with a high work function to collect the photoemitted electrons (Anode).

When the light will strike at the detector it will liberate electrons from the photocathode which will be instantaneously driven (due to the internal electric field created by the difference in the work functions) towards the positive electrode contact and induce an electric current in the device.

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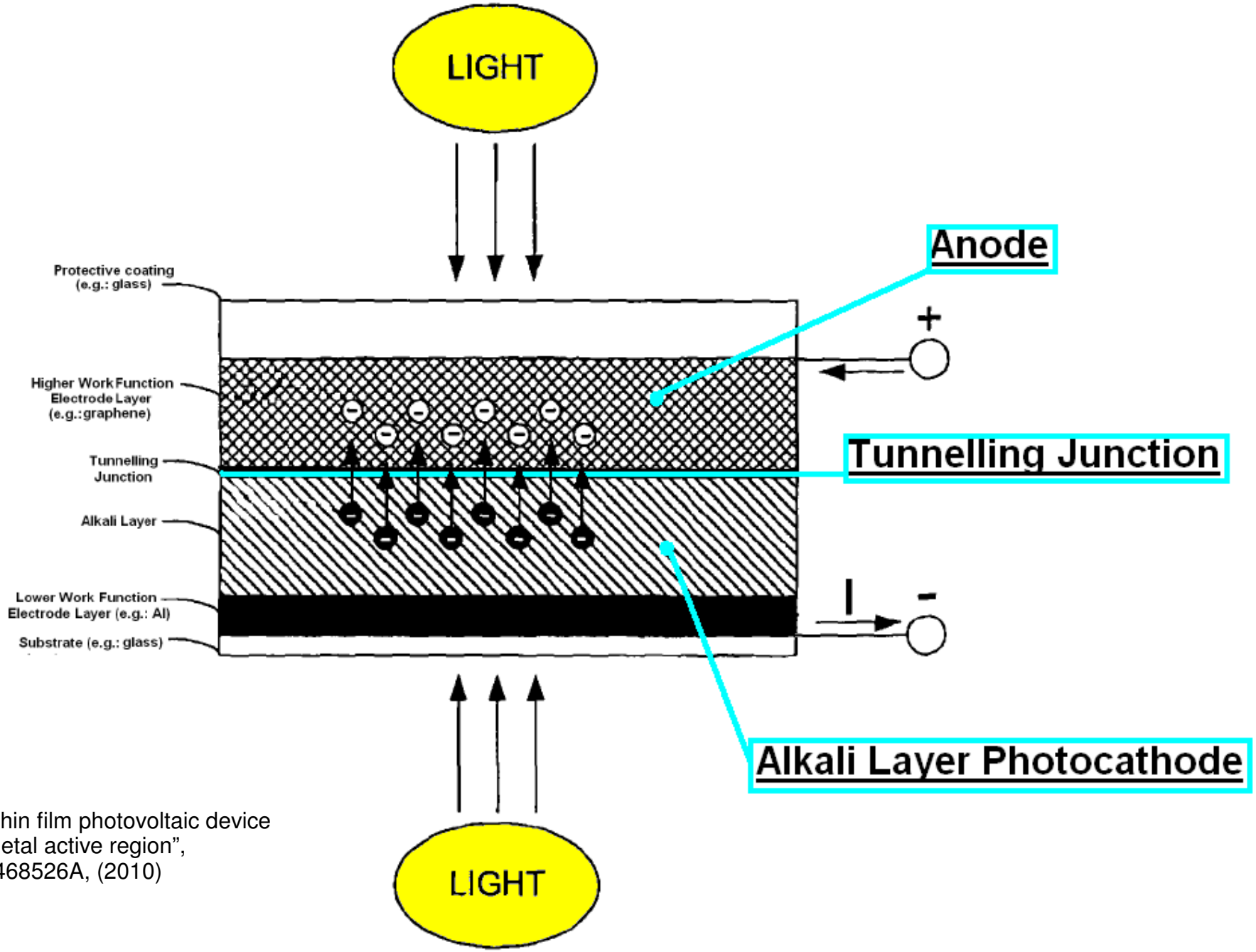
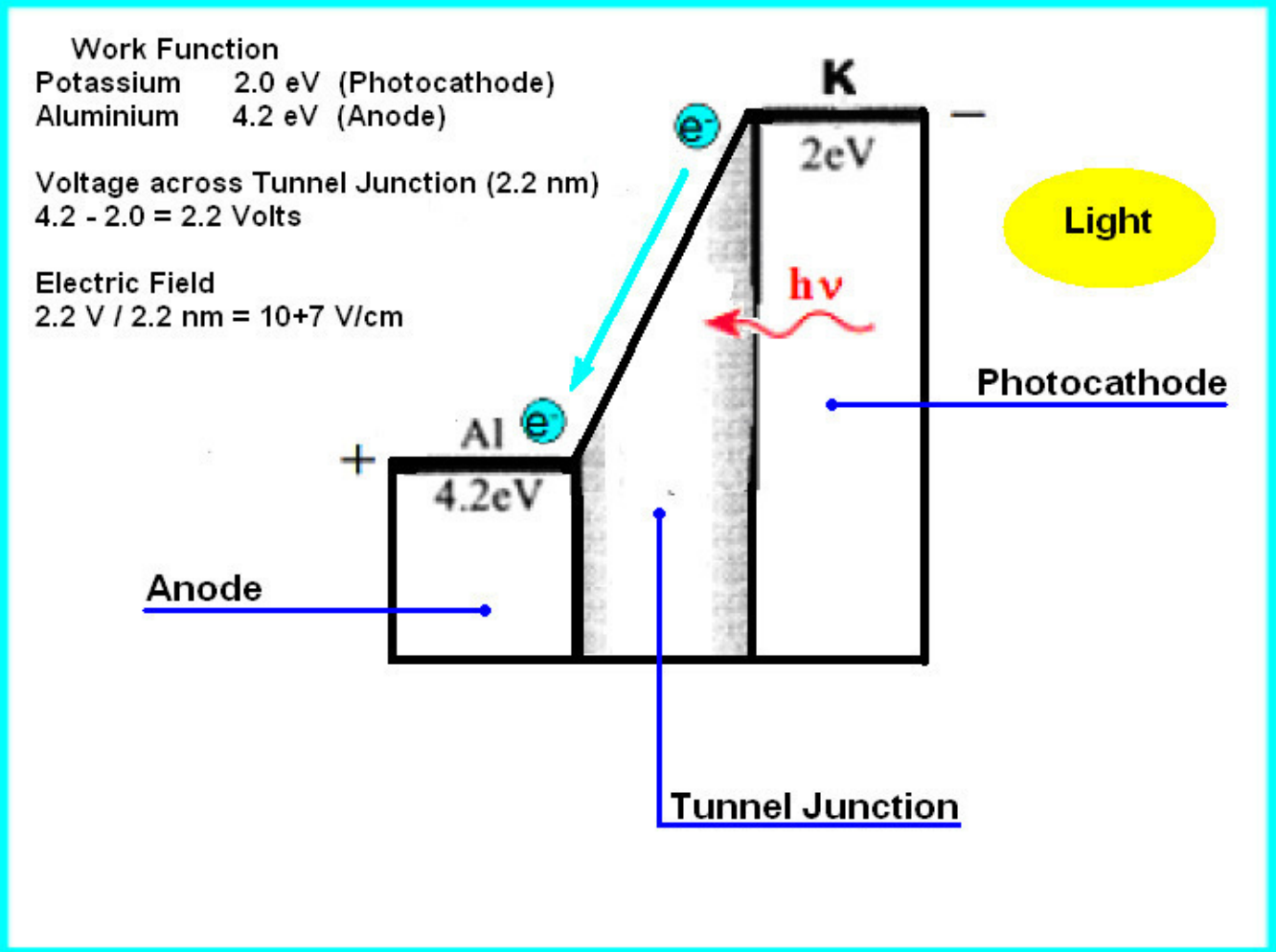


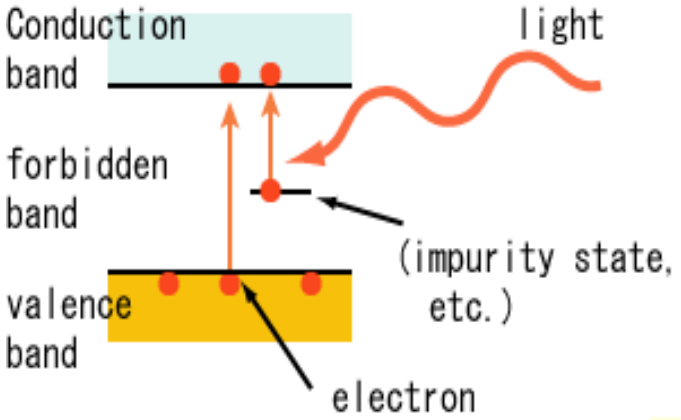
Galbiati, “a thin film photovoltaic device with alkali metal active region”, patent GB2468526A, (2010)

Figure 1 Sectional view of the structure of an ultra thin film photovoltaic device with alkali metal active region.

Photoinduced Electron Transfer

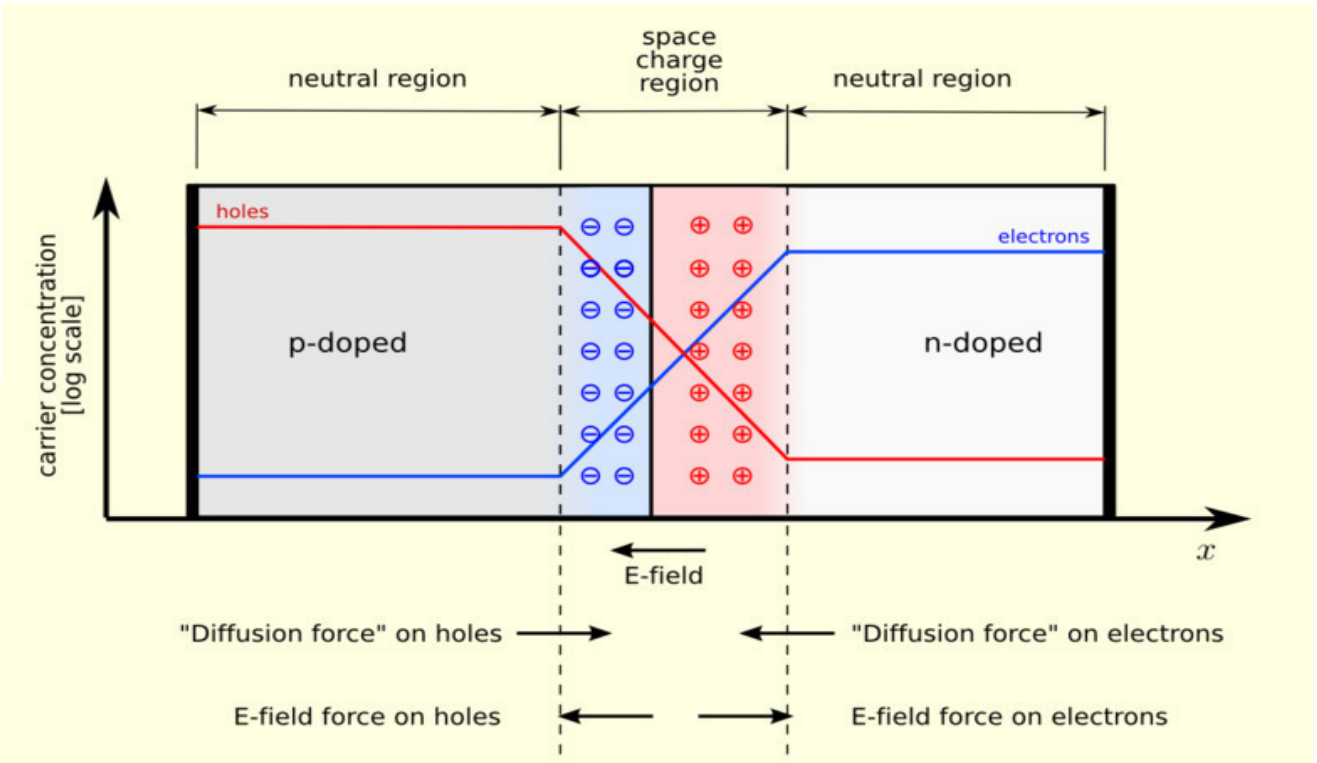


• Internal Photoelectric Effect: p-n junction



Silicon Band-Gap: 1.1 eV

http://en.wikiversity.org/wiki/File:Photoelectric-E.PNG



http://upload.wikimedia.org/wikipedia/commons/d/d6/Pn-junction-equilibrium.png

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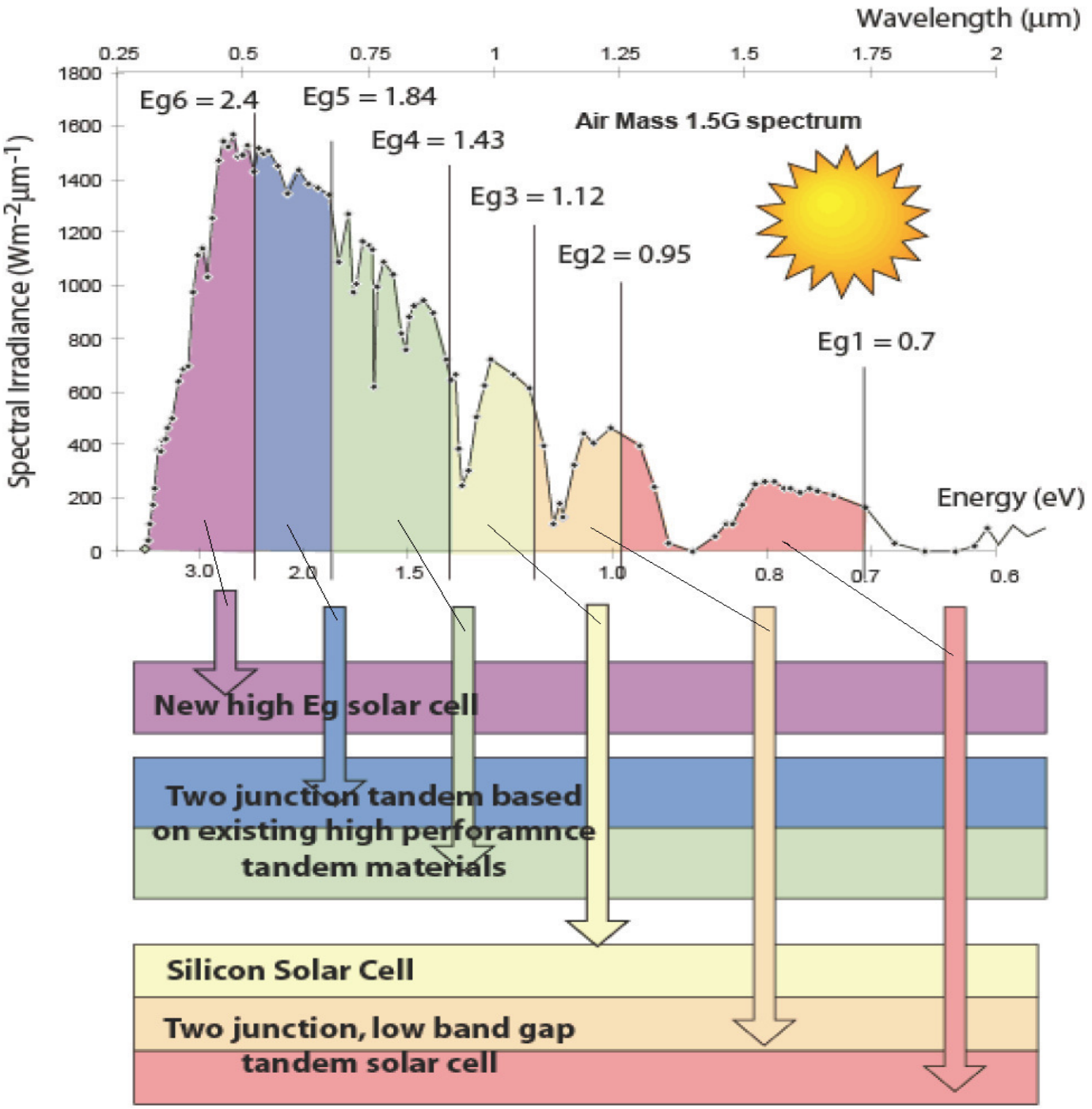
Wavelength (µm)
0.25
0.5
0.75
1
1.25
1.5
1.75
2
Spectral Irradiance (Wm-2µm-1)
1800
1600
1400
1200
1000
800
600
400
200
0
Eg6 = 2.4
Eg5 = 1.84
Eg4 = 1.43
Eg3 = 1.12
Eg2 = 0.95
Eg1 = 0.7
Air Mass 1.5G spectrum
Energy (eV)
3.0
2.0
1.5
1.0
0.8
0.7
0.6
New high Eg solar cell
Two junction tandem based on existing high perforamnce tandem materials
Silicon Solar Cell
Two junction, low band gap tandem solar cell

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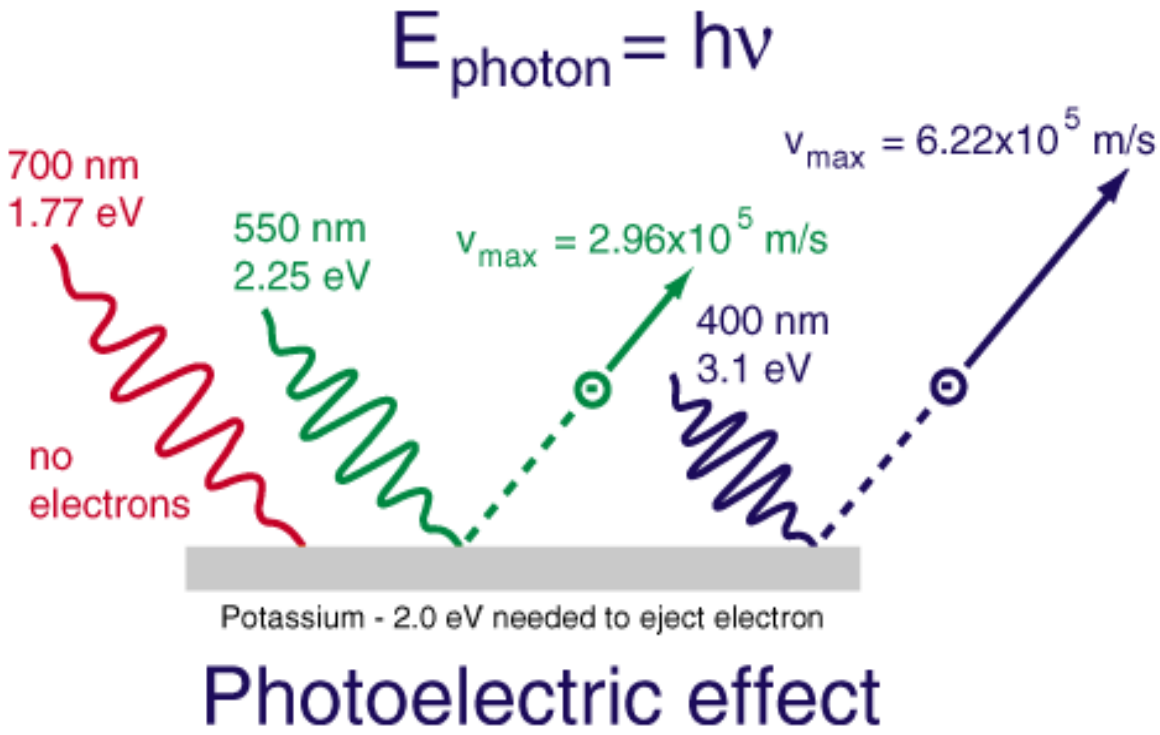
- **Photoelectric Effect: External**

- It is possible to remove electrons from any surface if photons have energy higher than the work function of the material:
- $\frac{1}{2}mv^2 = h\nu - W$
- W=Work Function



Albert Einstein , "*On a Heuristic Viewpoint Concerning the Production and Transformation of Light*",*Annalen der Physik* **17,** (1905) pp. 132–148

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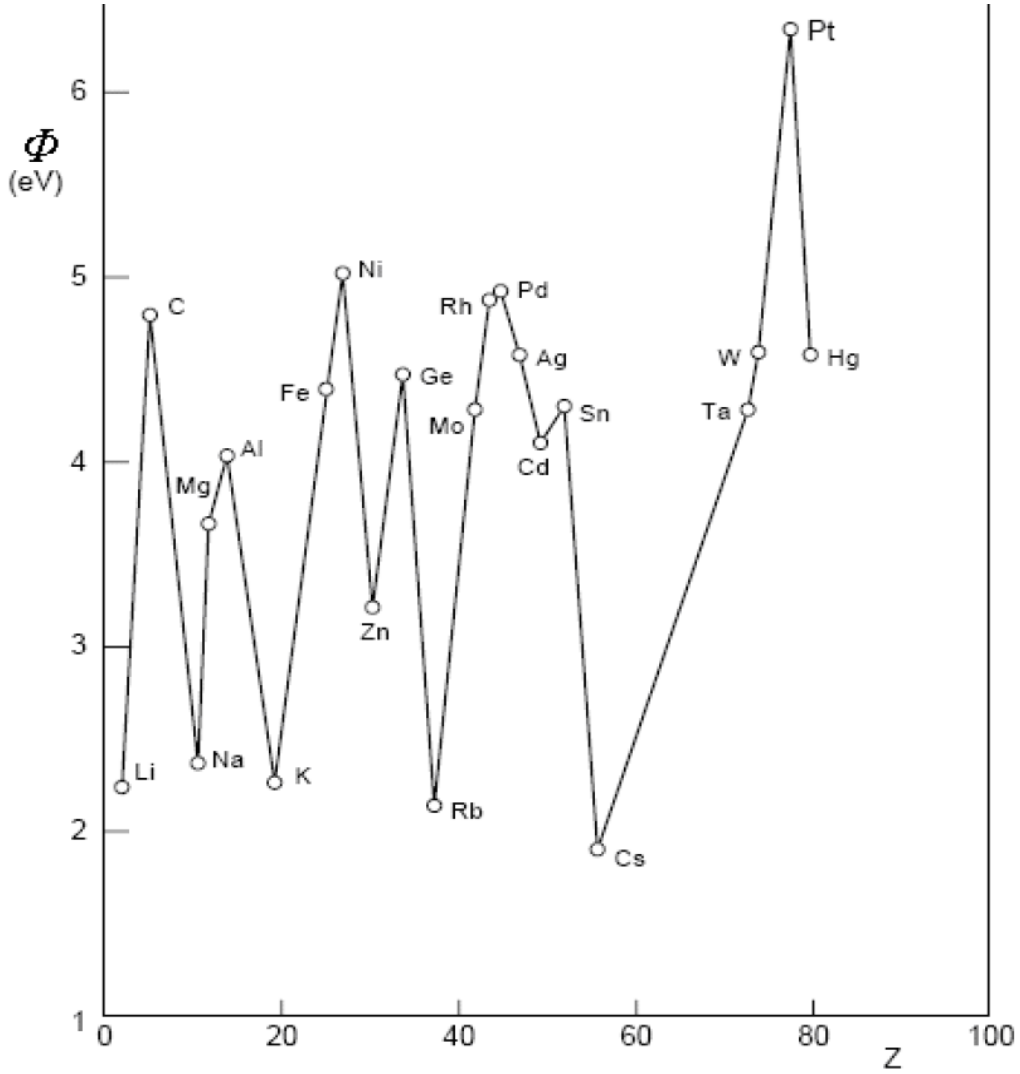
Work functions of pure metals, in order of atomic number



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A Novel Ultra Thin Film Photovoltaic Technology with Alkali Metal Active Region

Parent Technology (1): Vacuum Alkali Photocathodes

- **Employed as high sensitivity light detectors are able to directly convert visible light into electrical current with the highest quantum efficiency per volume of any material.**

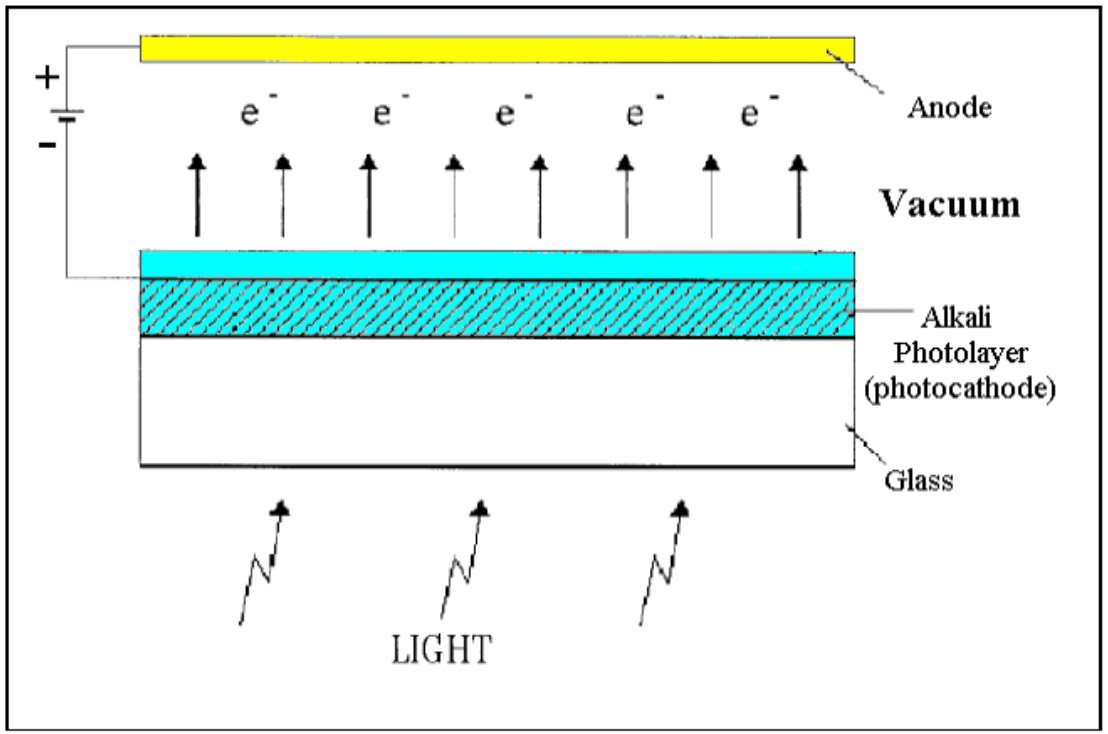

Figure 1 Vacuum Alkali Photocathode

Elster and Geitel, "On the discharge of negative electric bodies by sun and daylight", *Ann. Physik*, Vol. 38, pp. 497-514, 1889

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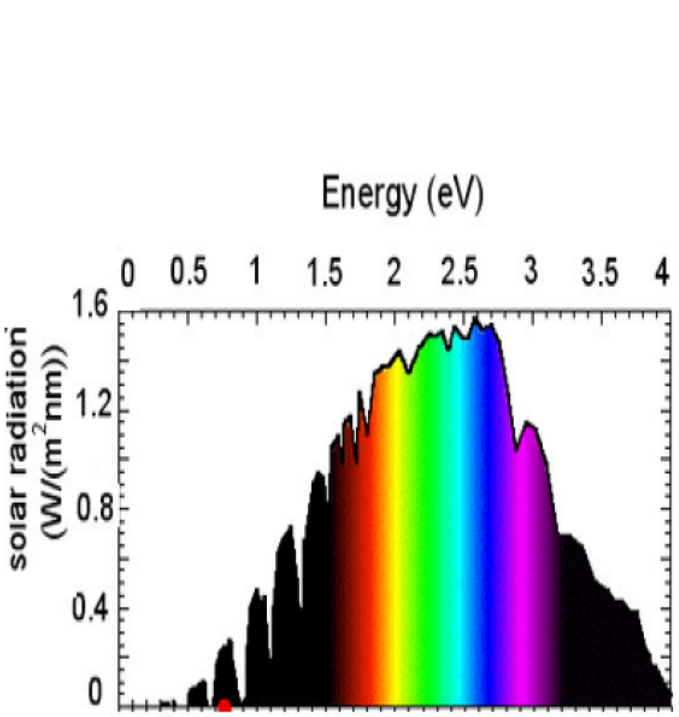
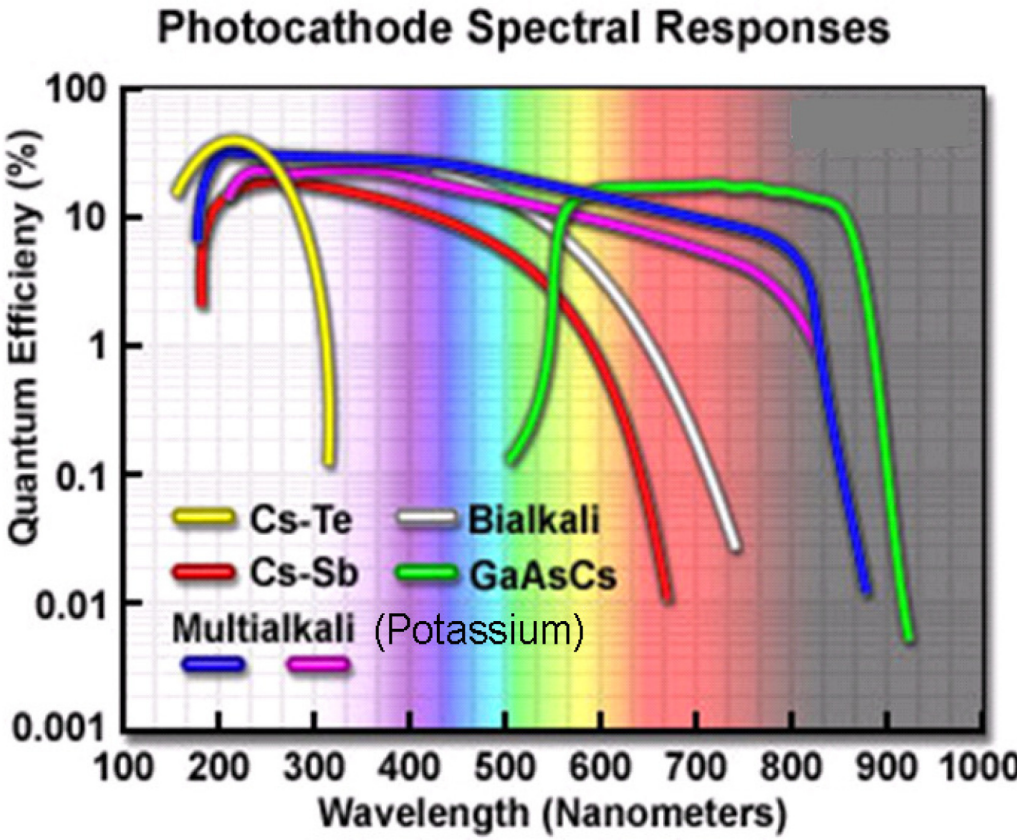
- **Photocathode Layer Quantum Efficiency**





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Electron Emission from Photocathode

The three main processes of the photocathode are [Spicer]:

1. **absorption of a photon and transfer of energy to an electron within the photoemissive material**

2. **migration of that electron to the surface**

3. **escape of the electron from the surface of the photocathode**

- **The energy that can be transferred from the photon to an electron in the first step is given by the quantum energy of the photon *hv.***

- **In step 2, some of the energy is lost through electron-electron interaction in the migration process.**

- **In step 3, there must be sufficient energy left for the electron to overcome the inherent potential barrier (the *work function*) that exists at the interface between the material and vacuum.**

Spicer, Modern Theory and Applications of Photocathodes, SPIE 1993 InternationalSymposium, San Diego 1993,

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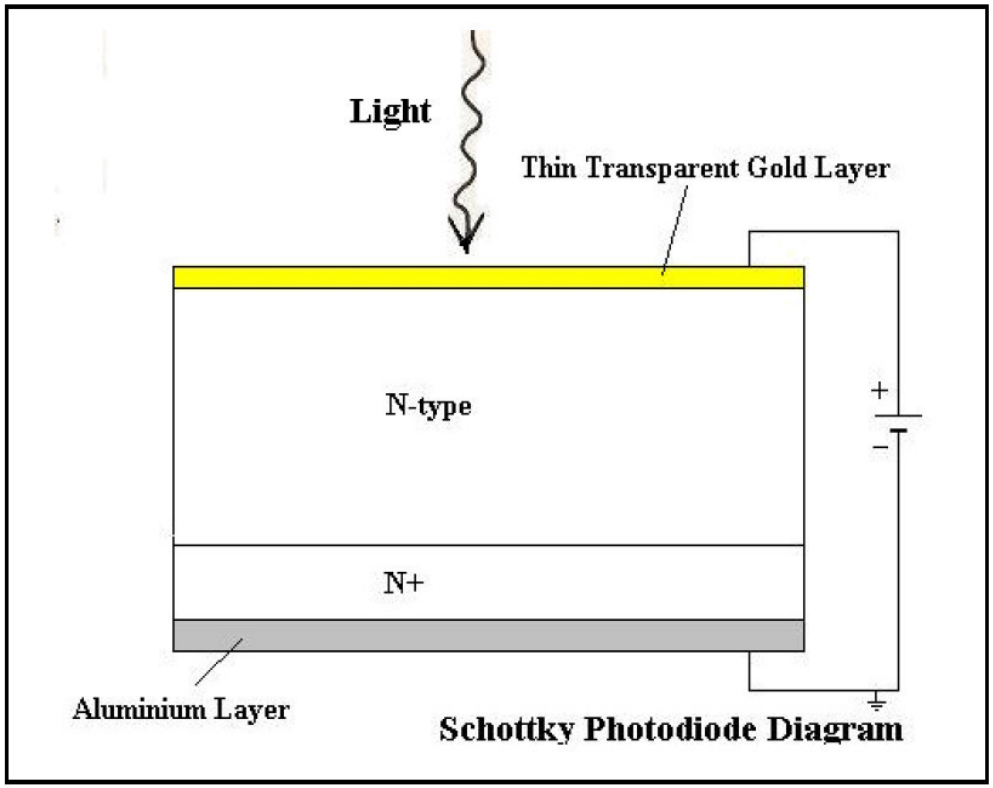
Parent Technology (2): Schottky Photodiode

The Schottky barrier photodiode is formed at a junction between a thin (< 20 nm) transparent and conducting gold metallic layer and a semiconductor. [see Wilson and Hawkes, p. 334].



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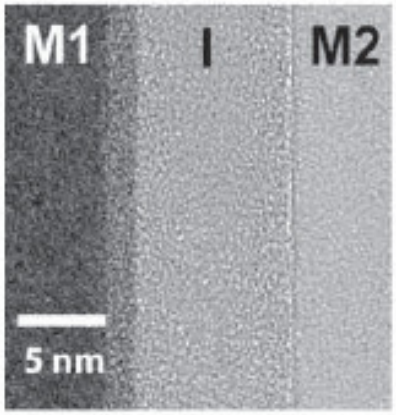
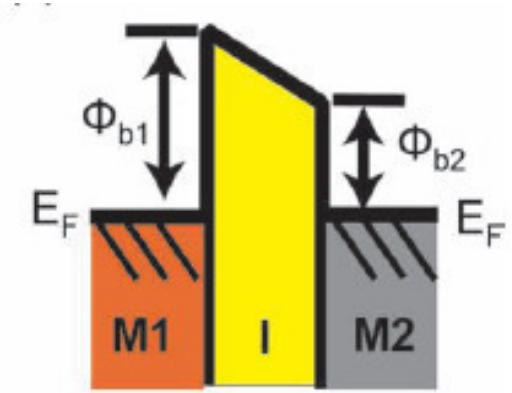
Parent Technology (3): Metal-Insulator-Metal (MIM) tunnel diodes

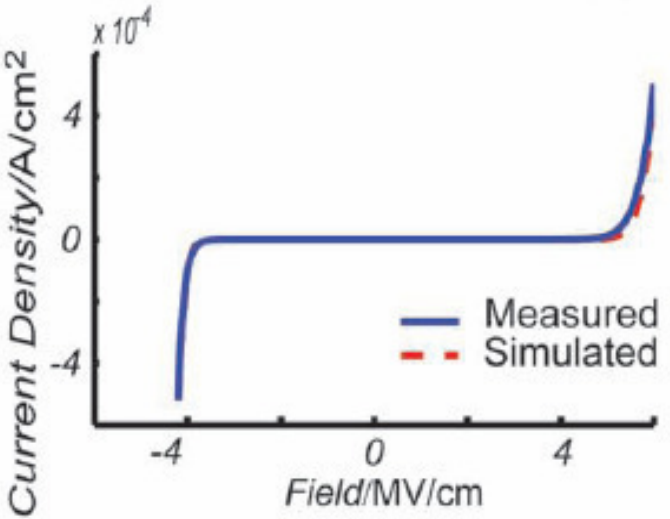
High-performance metal-insulator metal (MIM) diodes control quantum mechanical tunneling through an ultrathin dielectric. Such diodes are the basis for alternative approaches to conventional thin-film transistor technologies for large-area information displays, [1 , 2] various types of hot electron transistors, [2–6] ultrahigh speed discrete or antenna coupled detectors, [7–14] and optical rectennas. [15]



(d)



(e)



(f)

Cowell et al., ***Advancing MIM Electronics*** Adv. Mater. 2011, 23, 74–78

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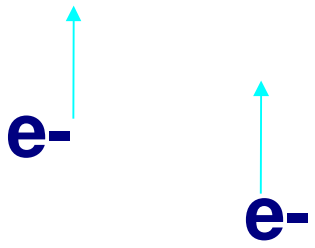
- **Ohmic Contacts / Volta Effect**

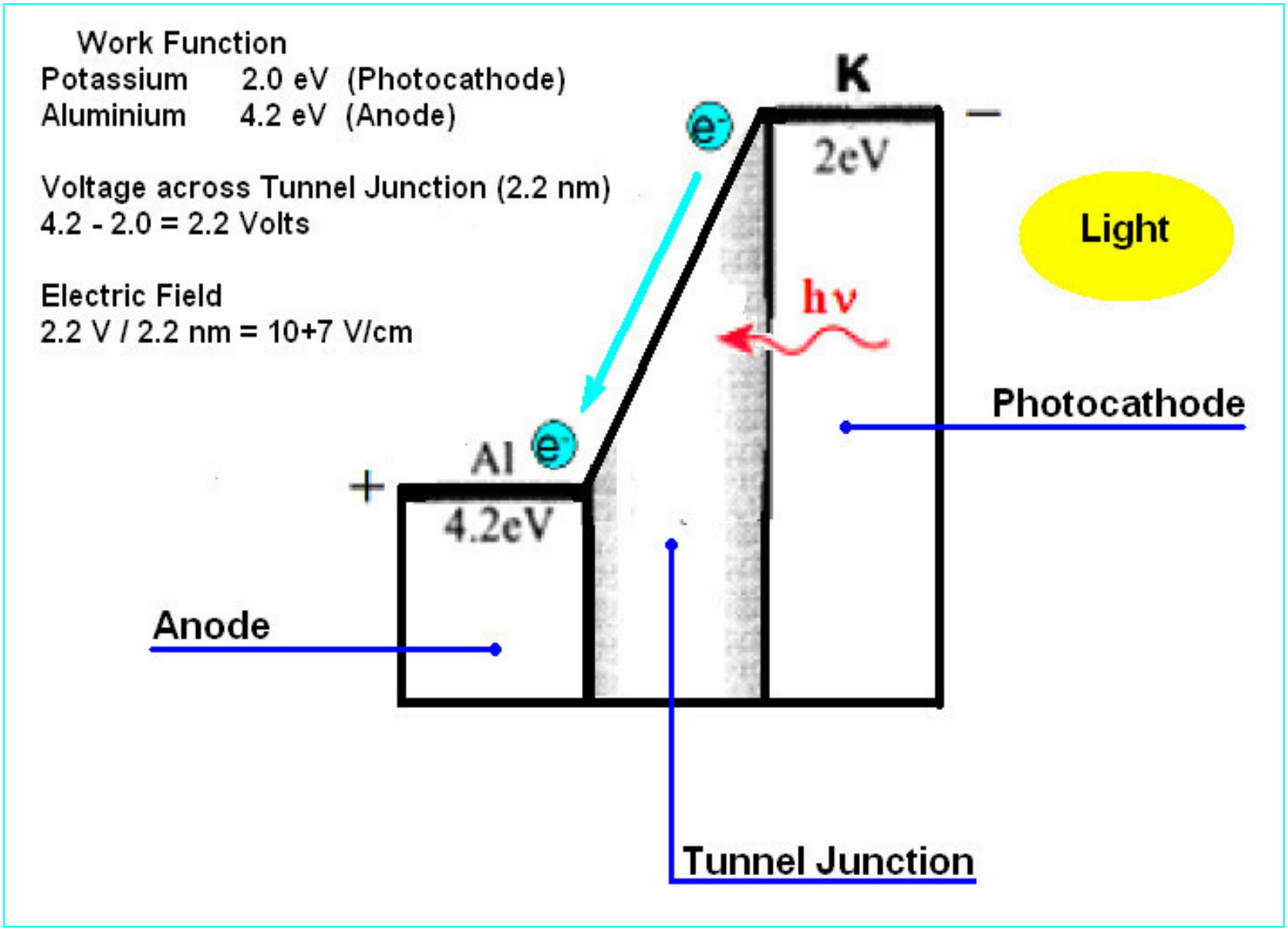
- **High Work Function Metal → Electron Extraction ("Hole Injection")**



- **Low Work Function Metal → Electron Injection ("Hole Extraction")**

Arnaldo Galbiati, admin@solaris-photonics.com

Photoinduced Electron Tranfer



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A Novel Ultra Thin Film Photovoltaic Technology with Alkali Metal Active Region

- **Gain Mechanism (1): Impact Ionization**
- **Avalanche Breakdown**
- **ZENER DIODE**

- **Avalanche breakdown occurs when the electric field across a junction has become so large that an electron can gain enough energy to break a bond when it collides with a lattice atom.**
- **Physically this means that the electron can ionize an atom (promote an electron from the valence to the conduction band) and generate an electron-hole pair.**
- **The electron-hole pair is now itself accelerated, generating more electron-hole pairs in the process.**
- **In a Zener diode the p-n junction is highly doped → the depletion width becomes small → a very high electric field at the junction → only very small increase in the Voltage → electrons are directly removed from their valence bonds.**

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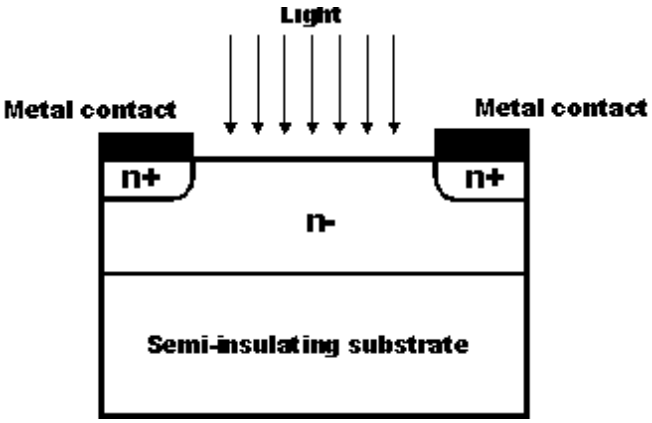
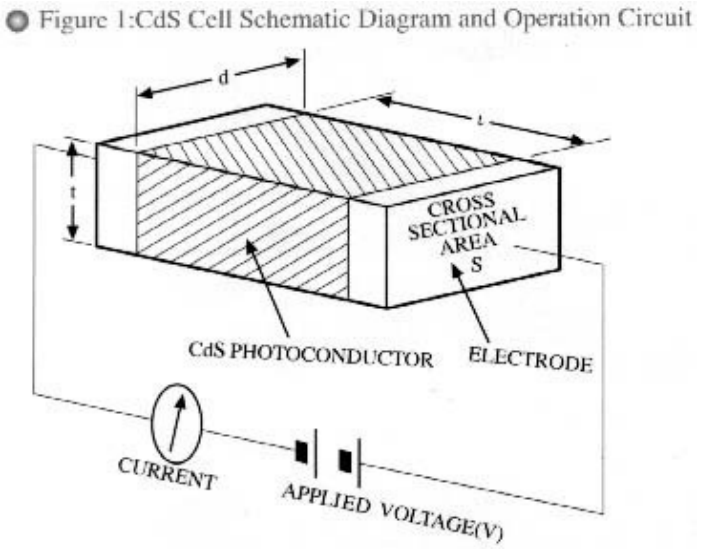
Parent Technology (4): Photoconductors-Photocells





http://www.octsensors.com/cds/p6-12.htm

Arnaldo Galbiati, admin@solaris-photonics.com

http://www.radio-electronics.com/info/data/resistor/ldr/light_dependent_resistor.php

Gain Mechanism (2): Photoconductive Gain

- A *photoconductive detector* consists of a sample of semiconducting material fitted with two injecting contacts (or "ohmic" contacts) at opposite surfaces.
- When a voltage is applied, a measurable current flows (the *equilibrium current*) determined by the free carrier concentrations.
- The free carrier concentration will be increased by irradiating the device with light (or any other type of ionizing radiation) resulting in an increase in the material conductivity.
- The induced photocurrent is $\propto$ energy deposited.
- With true injecting contacts every electron that exit one contact is replaced by the injected electron that enters through the opposite contact [R.H. Bube, *Photoconductivity in Solids*].

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- **Gain Mechanism (1): Photoconductive Gain**
- **Photocurrent/Photonductive gain is*:**

$$\text{Gain} = \frac{\text{carrier mobility} \times \text{carrier lifetime} \times \text{E-field}}{\text{Thickness}}$$

- **Carrier mobility x carrier lifetime = $\mu\tau$ product**

*** [R.H. Bube, *Photoconductivity in Solids*].**

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- **Gain Mechanism (1): Photoconductive Gain**
- **For a typical c-Si solar cell the gain is *:**

$$\text{Gain} = \frac{1500\ \text{cm}^2\,\text{V}^{-1}\,\text{s}^{-1} \times 10^{-8}\,\text{s} \times 20\ \text{V cm}^{-1}}{0.03\ \text{cm}} = 0.01$$

- **Carrier mobility x carrier lifetime = $\mu\,\tau$ product**

* [R.H. Bube, *Photoconductivity in Solids*].

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- **Gain Mechanism (1): Photoconductive Gain**

- **For a typical c-Si solar cell the gain in the depletion region is *: $G = \mu \tau E W^{-1}$**

- **Gain = $\dfrac{1500\ cm^2 V^{-1} s^{-1} \times 10^{-8} s \times 7*10^{+3} V\ cm^{-1}}{0.001\ cm} = 1050$**

- **Carrier mobility x carrier lifetime = $\mu \tau$ product**

- *** [R.H. Bube, *Photoconductivity in Solids*].**

A Novel Ultra Thin Film Photovoltaic Technology with Alkali Metal Active Region

- **Gain Mechanism (1): Photoconductive Gain**
  - **For the ultra thin film alkaline solar cell,**
- **choosing CdS layer (2.2 nm) with $\mu_e\tau_e = 5\cdot10^{-7}$ cm^2 V^{-1} [1]:**

$$\text{Gain} = \frac{5\cdot10^{-7}\ \text{cm}^2\ \text{V}^{-1} \times 5\cdot10^{+6}\ \text{V cm}^{-1}}{2.2\cdot10^{-7}\ \text{cm}} = 10^{+7}$$

- **Carrier mobility x carrier lifetime = $\mu\ \tau$ product**
- **Electric field = E Thickness= W** **([2] $G = \mu_e \tau\, \mathrm{E}\, W^{-1}$)**

[1] Gu et al. Nano Lett., 2006, 6 (5), pp 948–952 [2] R.H. Bube, *Photoconductivity in Solids*

A Novel Ultra Thin Film Photovoltaic Technology with Alkali Metal Active Region

- **Gain Mechanism (1): Photoconductive Gain**

- **For the ultra thin film alkaline solar cell, choosing a-Si:H layer (2.2 nm) with $\mu\tau = 10^{-7}$ cm^2 V^{-1} [1]:**

$$\text{Gain} = \frac{1 \cdot 10^{-7}\ \text{cm}^2\ \text{V}^{-1} \times 5 \cdot 10^{+6}\ \text{V cm}^{-1}}{2.2 \cdot 10^{-7}\ \text{cm}} = 2 \cdot 10^{+6}$$

- **Carrier mobility x carrier lifetime = $\mu\ \tau$ product ([2] $G = \mu_e \tau E W^{-1}$)**
- **Electric field = E Thickness= W**

[1] H. Okamoto et al,. J. Appl. Phys. $_{54}$, 3236 (1983) [2] R.H. Bube, *Photoconductivity in Solids*

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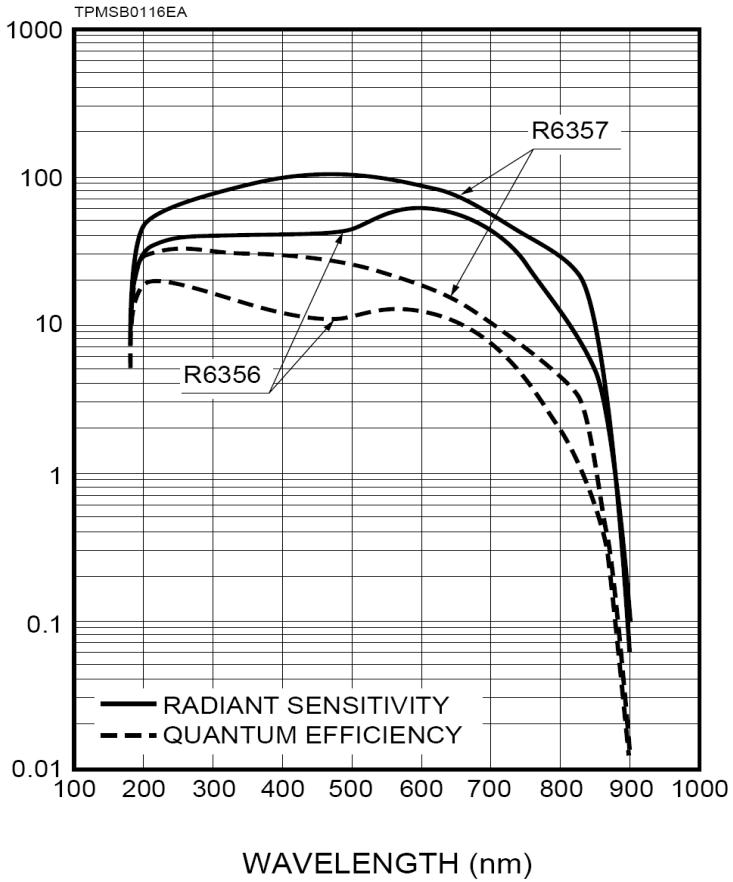
Alkali Photocathode Layer Quantum Efficiency

Typical Spectral Response of High Sensitivity MA



- Cathode Radiant sensitivity is the photoelectric current from the photocathode, divided by the incident radiant power at a given wavelength, expressed in A/W (amperes per watt)

- The radiant sensitivity at 300 to 700 nm :

~ 70 mA / W

/wwwphysics.ucsd.edu/neurophysics/lab/Hamamatsu_R6357_PMT.pdf

A Novel Ultra Thin Film Photovoltaic Technology with Alkali Metal Active Region

Ultra Thin Film Alkaline Solar Cell Efficiency:

- The applied voltage is the difference between the work functions of the metal electrode layers: **1 Volt (for W_f of K → 2.2 eV and Zn →3.2 eV)**
- With a tunnel junction thickness is **2.2 nm**
- The corresponding electric field is **$5 \cdot 10^{+6}$ V cm^{-1}**
- With input photocurrent from the alkali layer: **~ 70 mA / W**
- And tunnel junction material with **$\mu\tau = 5 \cdot 10^{-7}$ cm^2 V^{-1}**
- The theoretical photoconductive **Gain = 10.000.000 = 10^{+7}**
- Therefore the output current = **$7 \cdot 10^{+5}$ A/W**
- **And an efficiency >> 30%**

A Novel Ultra Thin Film Photovoltaic Technology with Alkali Metal Active Region

• Ultra Thin Film Alkaline Solar Cell Efficiency:

- Clearly in real devices the enormous amount of current would be destructive
- Therefore the gain has to be decreased to a value 10-100
- with a current output of 0.7 A/W to 7 A/W → ~30% to 300% efficiency

(c-Si ~ 0.3 A/W at ~15% efficiency)

- This can be done by reducing the applied voltage → the difference between the work functions of the metal electrode layers.
- With a tunnel junction thickness larger than **2.2 nm**
- And corresponding electric fields < **$5 \cdot 10^{+6}$ V cm^{-1}**
- With less input photocurrent from the alkali layer: < **70 mA / W**
- And tunnel junction material with **$\mu\tau < 5 \cdot 10^{-7}$ cm^2 V^{-1}**

A Novel Ultra Thin Film Photovoltaic Technology with Alkali Metal Active Region

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- **Conclusions:**

- **A novel photovoltaic technology has been proposed that can exhibit an efficiency higher than 100%.**

- **The new devices stem from current technologies and are easy to fabricate and cheaper.**

- **This opens the way for a much cheaper type of solar cells: the "Alkaline Solar Cells"**

- **THANK YOU**

When the insulator has dissimilar electrodes connected to its surfaces, it is clear that the interfacial potential barriers differ in energy by an amount

$$(\psi_{m2}-\chi)-(\psi_{m1}-\chi)=\psi_{m2}-\psi_{m1}$$

as shown in figure 4(f). Thus a uniform intrinsic field F_{in} of strength $(\psi_{m2}-\psi_{m1})/es$ exists within the insulator. The origin of this zero-bias intrinsic field is a consequence of charge transfer *between* the electrodes. The electrode of lower work function, electrode 1, transfers electrons to electrode 2, so that a positive surface charge appears on electrode 1 and a negative surface charge on electrode 2. The amount of charge Q transferred between the electrodes (the surface charge on the electrodes) is

$$Q=\frac{(\psi_{m2}-\psi_{m1})\,AK\epsilon_0}{es}$$

where A is the electrode area.

Table 1. Depth of depletion region for several values of N_d

N_d (cm^{-3})	10^{15}	10^{17}	10^{19}	10^{21}
λ (cm)	10^{-4}	10^{-5}	10^{-6}	10^{-7}

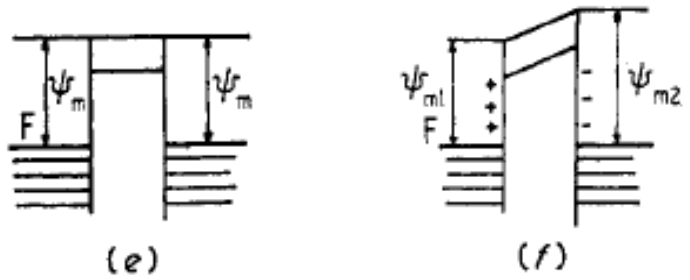
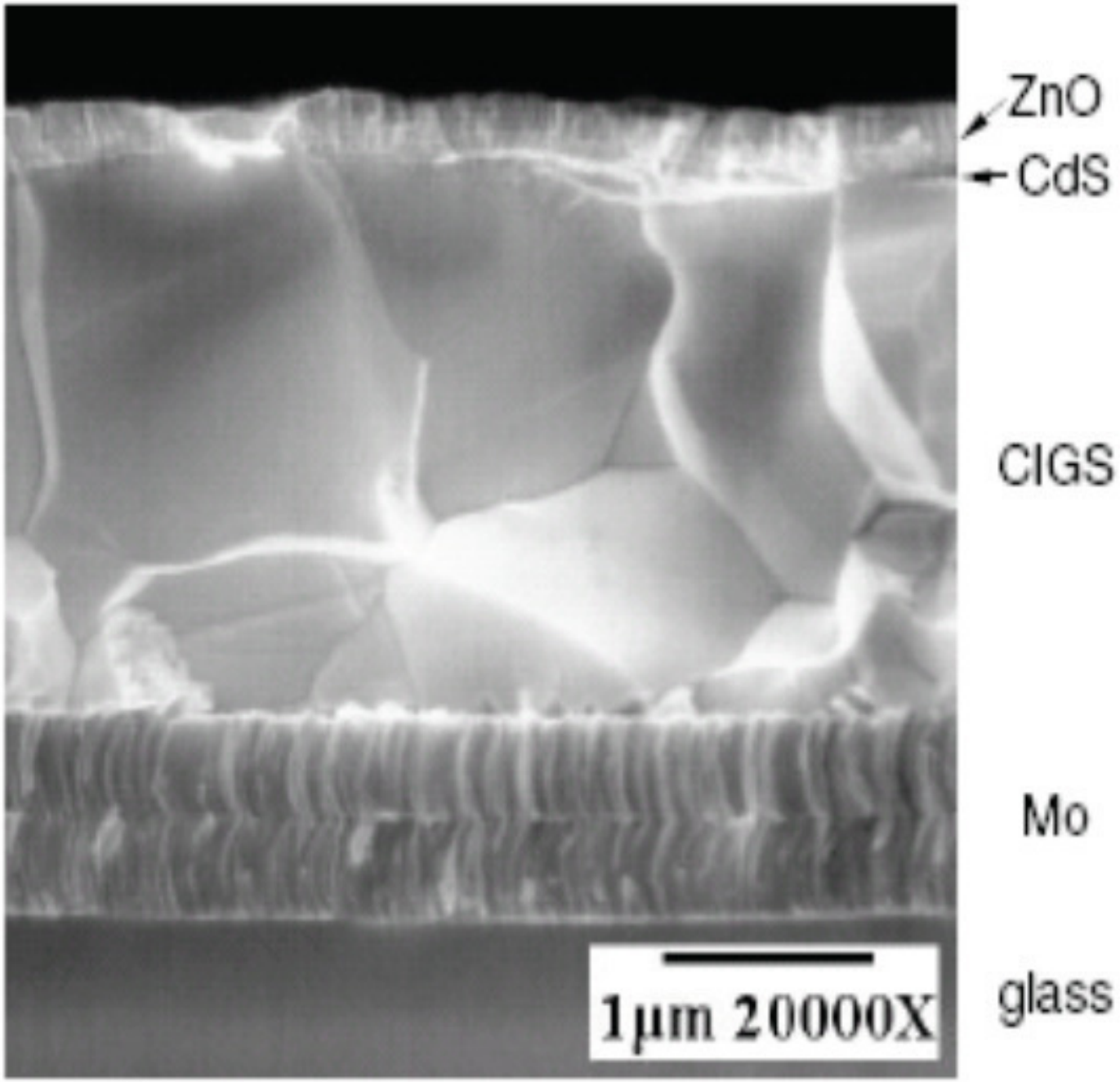


Figure 4. Energy diagrams of two metal contacts on an insulator. (a) and (b) represent imperfect and good ohmic contacts, respectively, (c) and (d) imperfect and good blocking contacts and (e) and (f) similar and dissimilar neutral contacts.

Sommer, Conduction in Thin Dielectric Films, J.Phys. D: Appl. Phys., 1971, Vol. 4

CIGS Thin Film Solar Cells



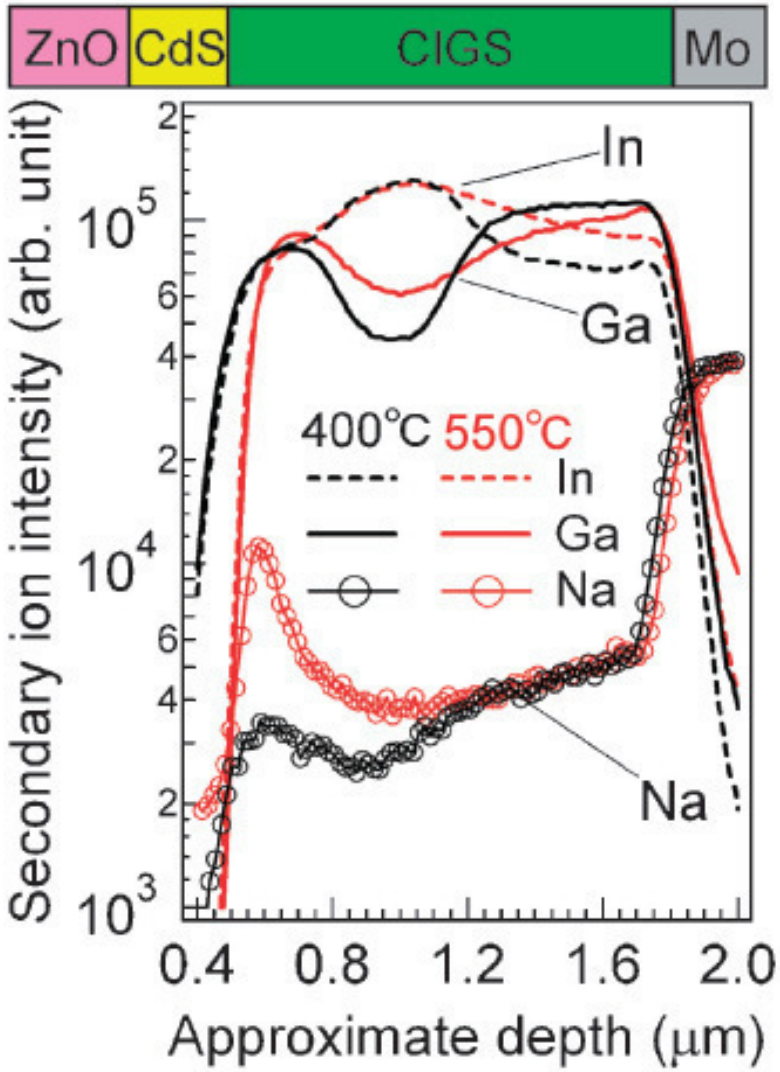


Fig. 2. SIMS depth profiles of elemental In, Ga, and Na distributions for CIGS layers grown on SLG substrates at the maximum substrate temperatures of 400 and 550 °C.

S. Ishizuka *et al.*

Appl. Phys. Express **1** (2008) 092303

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Manufacturing Steps c-Silicon Solar Cells

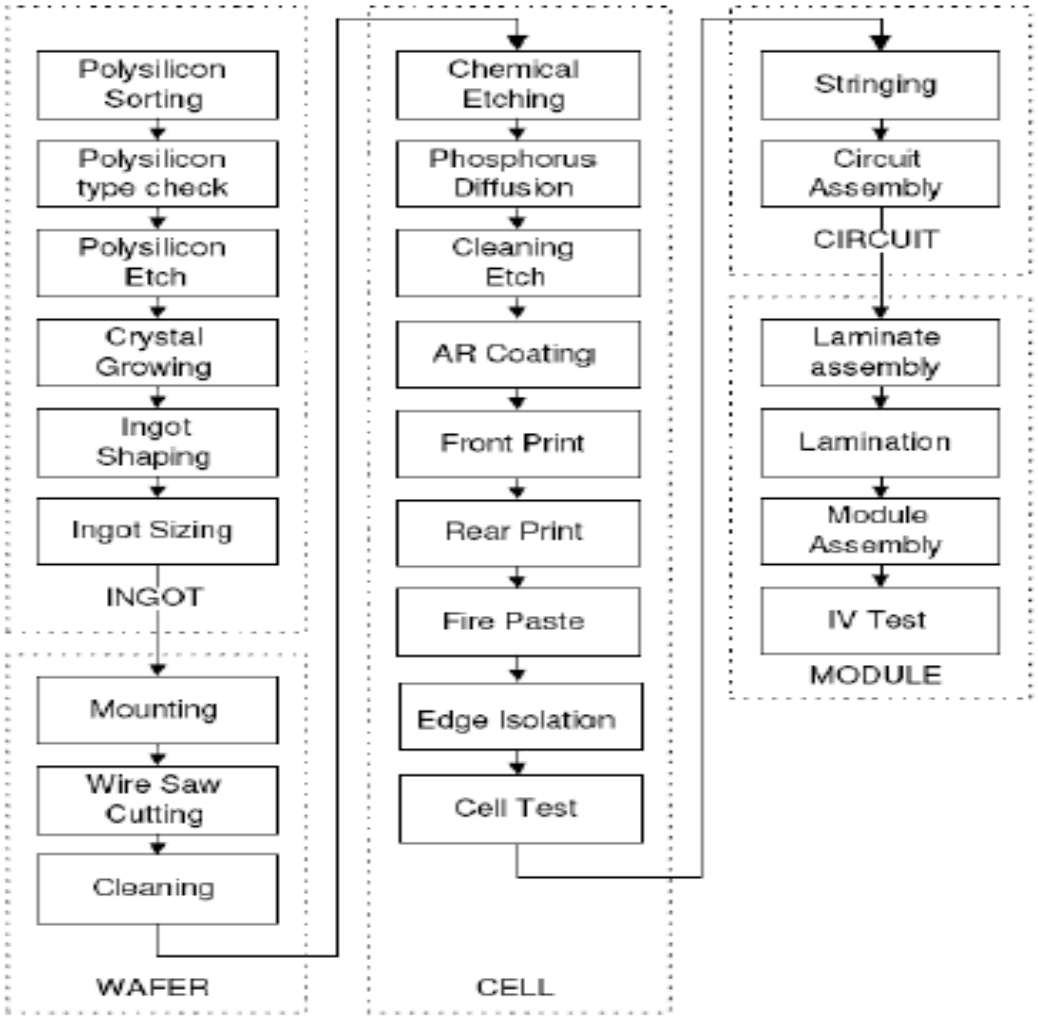
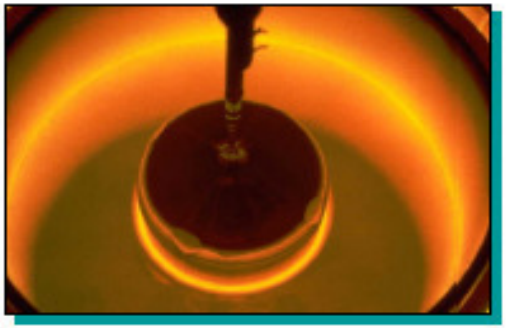
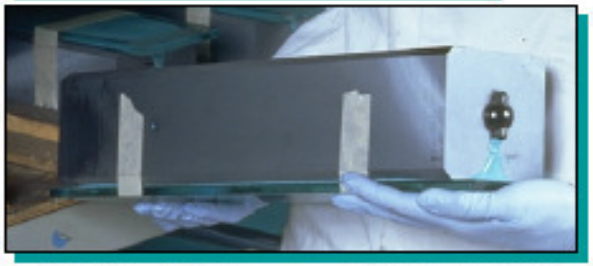


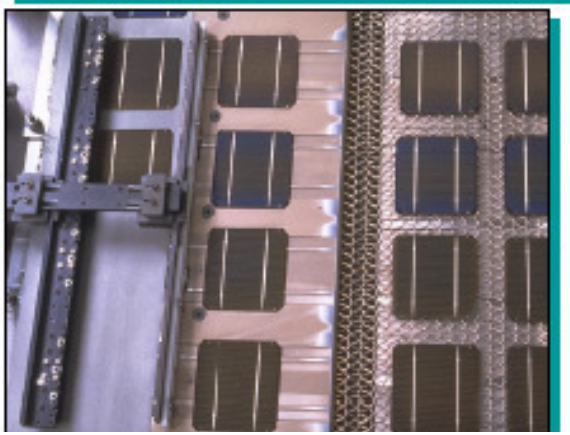
Figure 2. Process sequence for manufacturing crystalline silicon modules



Ingot growth



Shaped ingot



Cells in process

Arnaldo Galbiati, admin@solaris-photonics.com

Manufacturing Steps CIGS Solar Cells

METHOD FOR MANUFACTURING CIS-BASED THIN FILM SOLAR CELL

Patent Application Publication
Hakuma et al.

(10) Pub. No.: US 2010/0210064 A1
(43) Pub. Date: Aug. 19, 2010

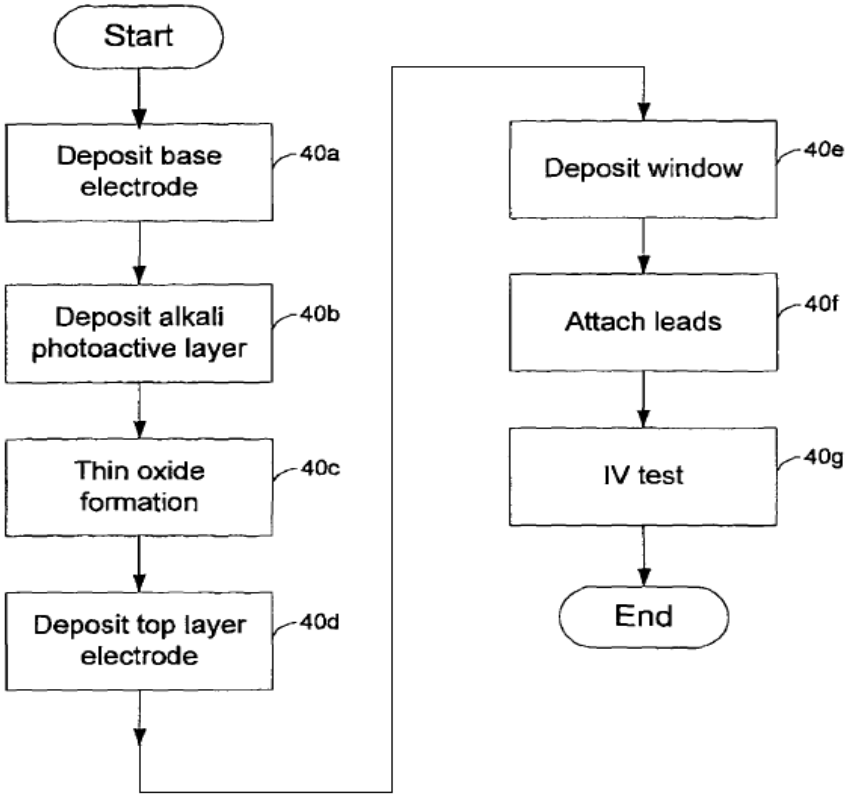
Assignee: **Showa Shell Sekiyu K.K.**, Tokyo (JP)

TABLE 1

Process conditions	
Glass substrate 1	High strain point glass (PD200, manufactured by Asahi Glass Co., Ltd.)
Metal backside electrode layer 2	Formed by sputtering of Mo. Film thickness - 0.5 μm. Na Concentration is stated separately.
P-type light absorbing layer 3	After forming a metal precursor film, selenization/sulfurization is performed to form Cu(InGa) $(SSe)_2$. Film thickness - 1.5 μm Cu/III = 0.9, Ga/III = 0.3 Selenization = 400° C. × 30 min., volume concentration of H_2Se - 5% sulfurization = 550° C. × 30 min., volume concentration of H_2S - 15%
N-type high resistance buffer layer 4	CBD method Zn (O, S, OH) Film thickness - 30 nm
N-type transparent and electroconductive window layer	MOCVD method ZnO:B Film thickness - 1.3 μm

A Novel Ultra Thin Film Photovoltaic Technology with Alkali Metal Active Region

Manufacturing Steps Novel “Alkaline Solar Cells”



Galbiati, “a thin film photovoltaic device with alkali metal active region”, patent GB2468526A, (2010)

Arnaldo Galbiati, admin@solaris-photonics.com

Table 1
Properties of diamond, silicon and gallium arsenide at 293 K.

Properties	Diamond	Silicon	GaAs
Density (g/cm^3)	3.5	2.33	5.32
Band gap (eV)	5.5	1.12	1.43
Resistivity (Ω cm)	$> 10^{11}$	2.3×10^5	1×10^8
Breakdown voltage (V)	10^7	3×10^5 (pn junction)	4×10^5
Electron mobility (cm^2 V/s)	2400	1350	8500
Hole mobility (cm^2 V/s)	2100	480	400
Saturation velocity (μ/ns)	220	82	80
Dielectric constant	5.7	11.9	13.1
Energy to form electron hole pair (eV)	13	3.6	4.2
Atomic charge	6	14	31.33
Average minimum ionising particle signal in 100 μm (electrons)	3600	9200	13 000

Comparison of electron mobility–lifetime products for materials considered for nuclear applications

"Detector grade" material	Mobility–lifetime product for electrons ($\mu\tau$) (cm^2/V)
Si	1
CZT	10^{-2}
CdTe	10^{-3}
SiC	10^{-4}–10^{-5}
GaAs	10^{-6}
CVD diamond (pc)	10^{-6}

■SPECTRAL RESPONSE CHARACTERISTICS