太陽光電鈍化技術

Passivation Technology for Photovoltaics

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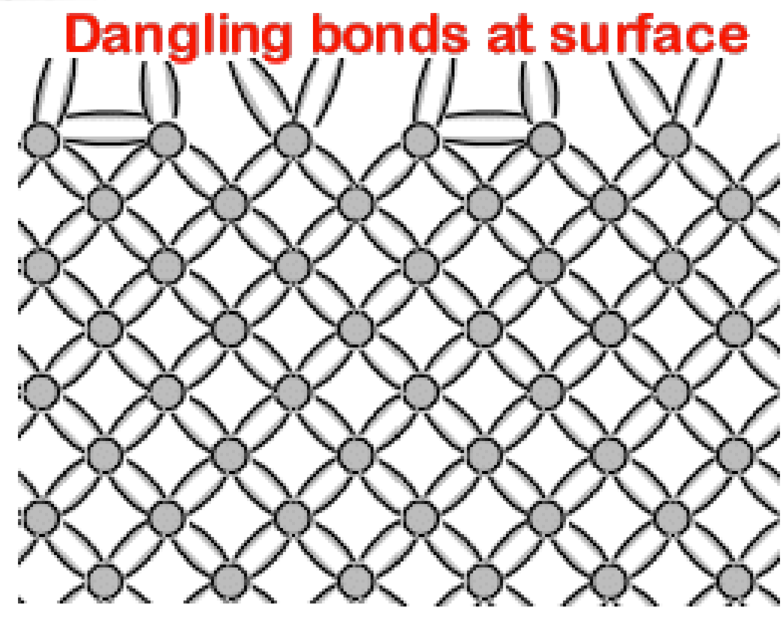
Outline

- Introduction
- Passivation Technologies
- GO for Solar Cell Passivation
- GO for Solar Water Splitting
- Summary

Why Passivation(鈍化)?

Recombination Occurs at surface



Rear Surface Recombination Dominates

- 太陽電池(矽)的表面
=>矽晶格的邊界(晶格嚴重的終結)
=>成為高復合的所在處
- 傳統(Al BSF)太陽電池遭受矽與其下金屬介面高表面復合速率(S_{back})所害

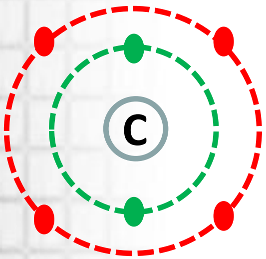
Ref.: http://www.pveducation.org/
S. W. Glunz, *Advances in OptoElectronics*

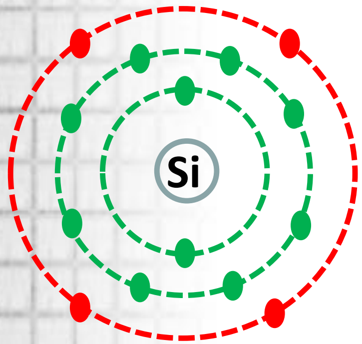
半導體常見元素

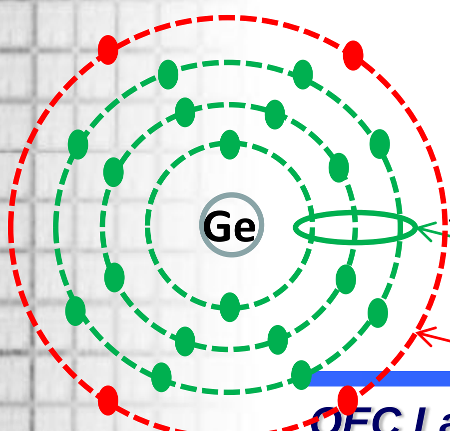
三族（有三個價電子）

四族（有四個價電子）

五族（有五個價電子）







A portion of the periodic table showing elements used in semiconductor materials

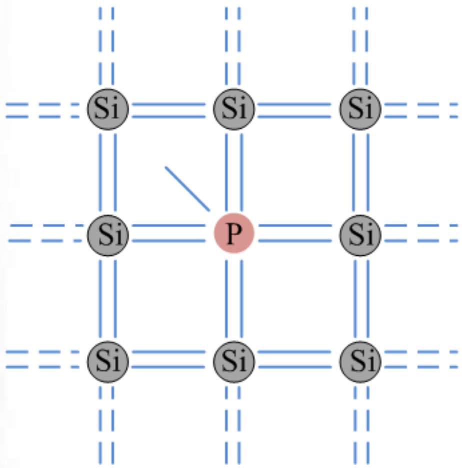
Group / Period	II	III	IV	V	VI
2		B Boron	C Carbon	N Nitrogen	O Oxygen
3		Al Aluminum	Si Silicon	P Phosphorus	S Sulfur
4	Zn Zinc	Ga Gallium	Ge Germanium	As Arsenic	Se Selenium
5	Cd Cadmium	In Indium	Sn Tin	Sb Antimony	Te Tellurium
6	Hg Mercury				

核心電子：穩定(之後不畫出)

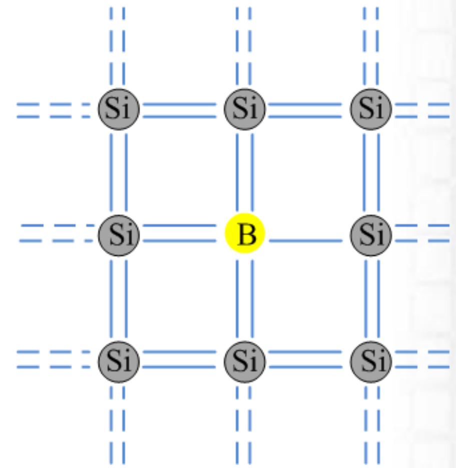
價電子:化學反應/共價鍵都靠它們

在四族半導體內摻三/五族元素

n型半導體(摻五族)



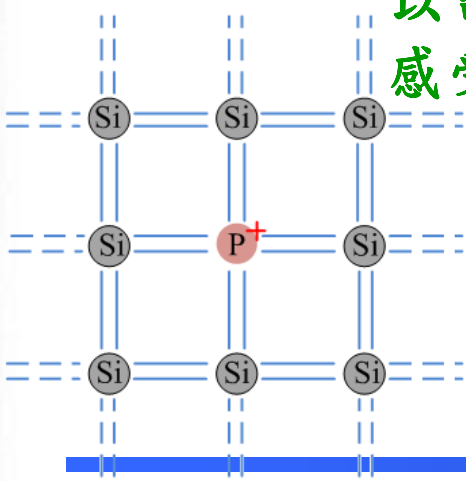
p型半導體(摻三族)

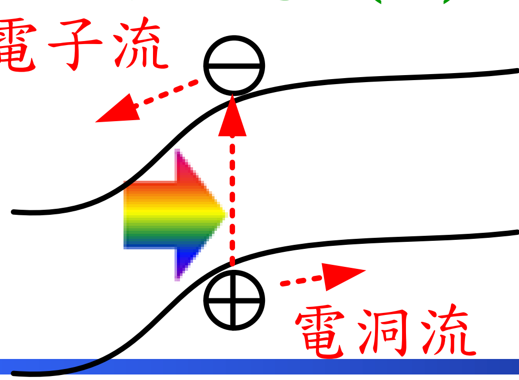


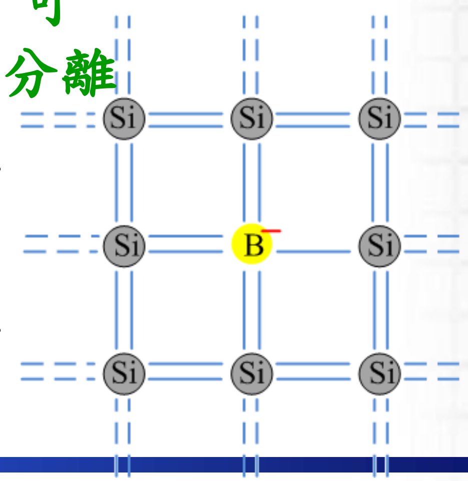
電子跑走，留下帶正電P離子

電洞跑走，留下帶負電B離子

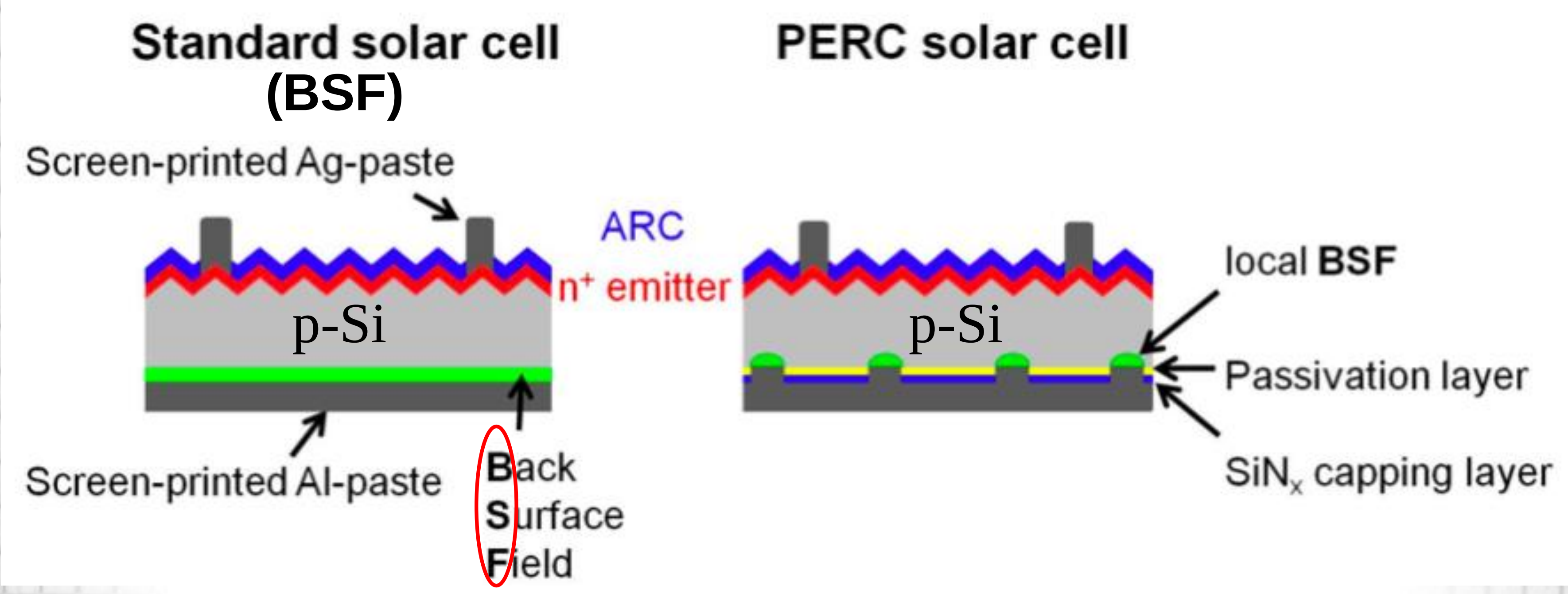
以電子觀點畫出能帶圖，可感受照光產生電子(洞)能分離





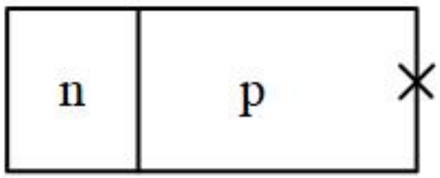


pn太陽電池架構早期採BSF，目前多改PERC



Ref.: https://www.solarchoice.net.au/blog/news/perc-solar-cells-steadily-gaining-steam-in-pv-160215

結構視角



能帶視角

爸爸視角

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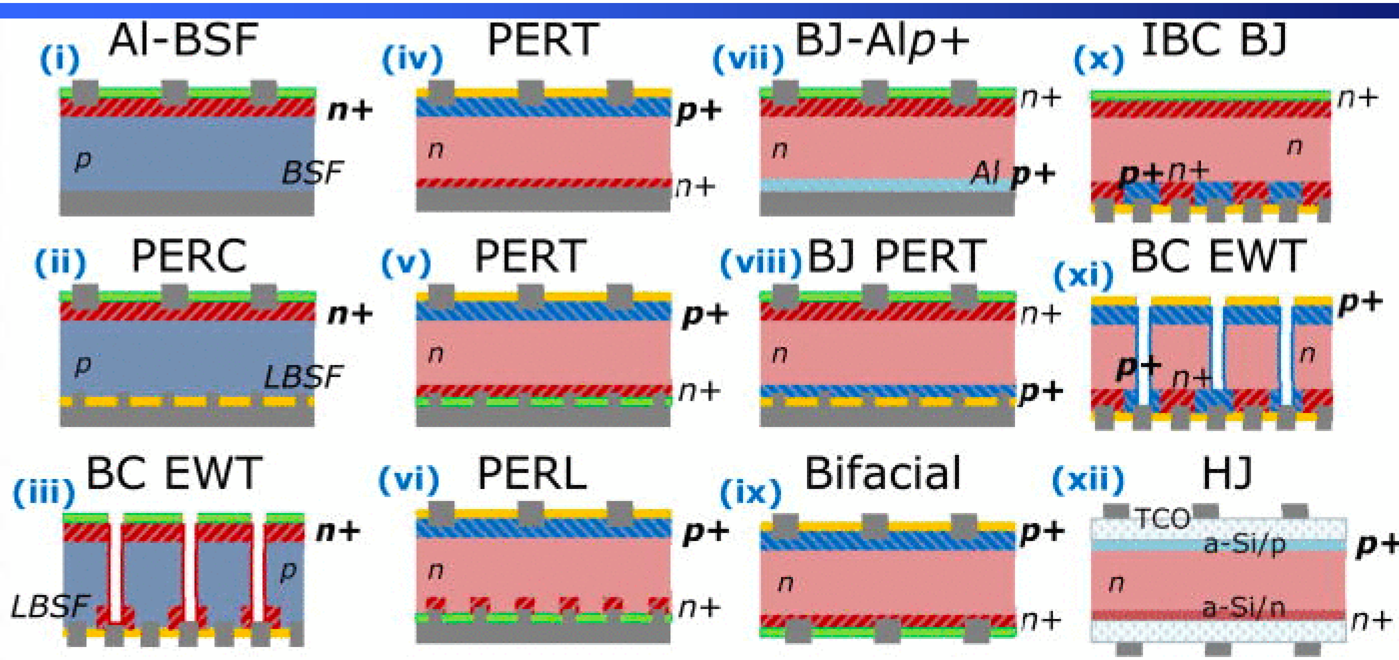
Cell技術千百種，要關注哪一種?

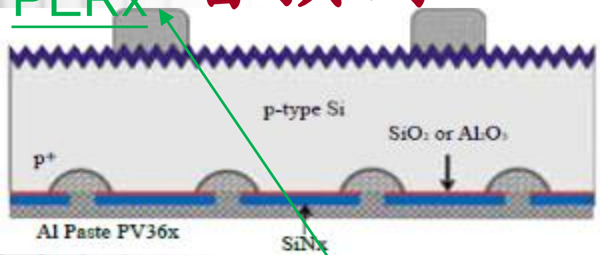


Various solar cell concepts based on *p*- and *n*-type Si wafers. (i) Full Al-BSF; (ii) passivated emitter and rear (PERC) cell; (iii) backcontacted emitter wrap through (BC EWT) cell; (iv), (v) passivated emitter and rear totally diffused (PERT) cell; (vi) passivated emitter and rear locally diffused (PERL) cell; (vii) backjunction Al alloyed rear emitter ("BJ-Al*p*+") cell; (viii) backjunction PERT cell; (ix) bifacial cell; (x) interdigitated backcontacted backjunction (IBC BJ) cell; (xi) backcontacted emitter wrap through (BC EWT) cell; (xii) heterojunction (HJ) cell.

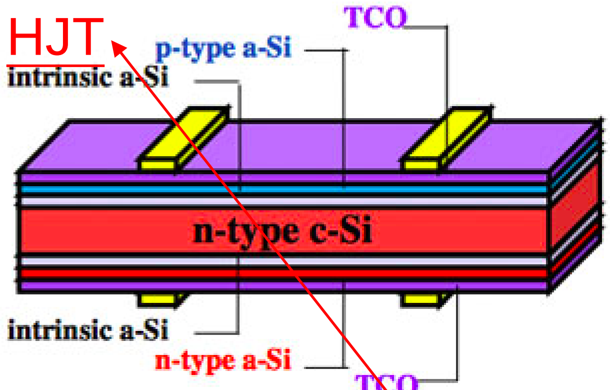
Ref:http://doi.org/10.1116/1.4728205

看預測

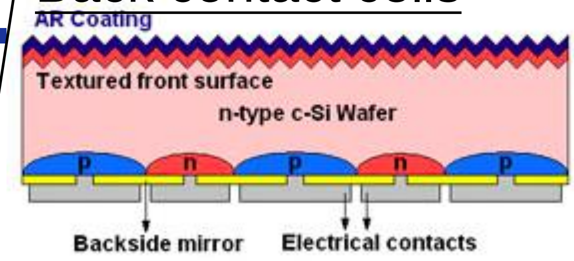
PERx

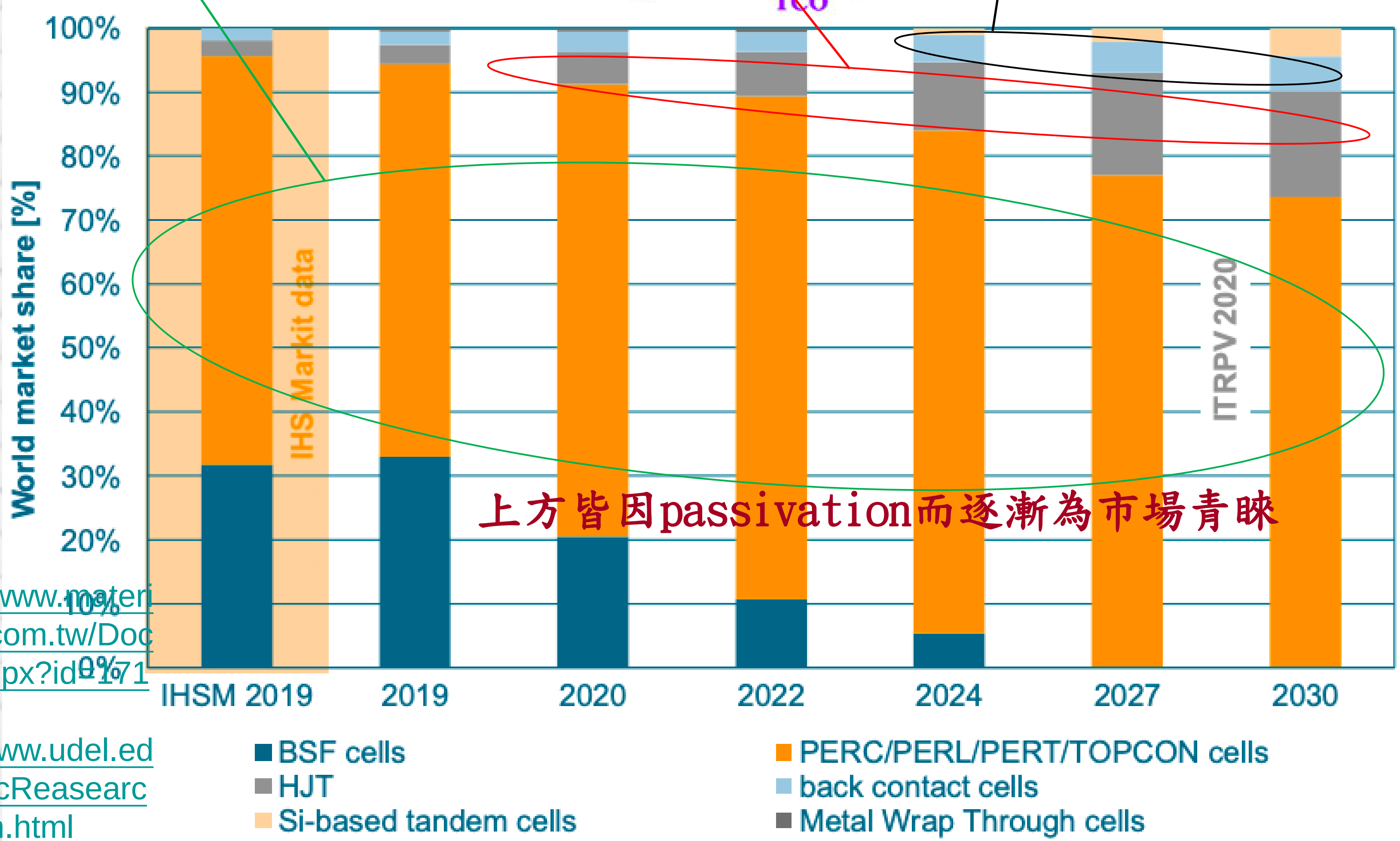


HJT



Back contact cells

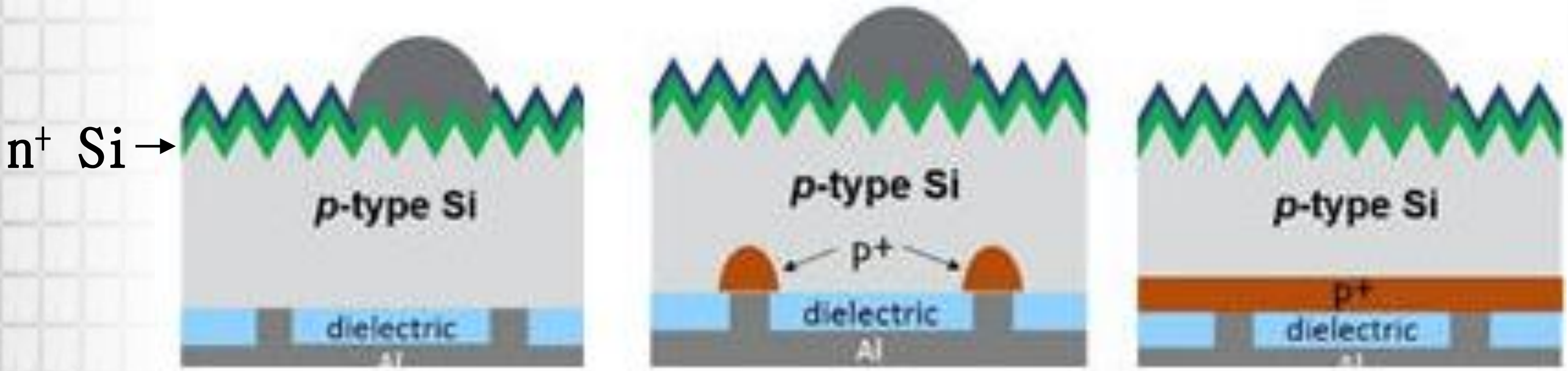




上方皆因passivation而逐漸為市場青睞

Ref.:
https://www.materialsnet.com.tw/DocPrint.aspx?id=17107
http://www.udel.edu/iec/iecReasearchSilicon.html

PERx Series



PERC (Passivated Emitter and Rear Contact)

PERL (Passivated Emitter and Rear Locally diffused)

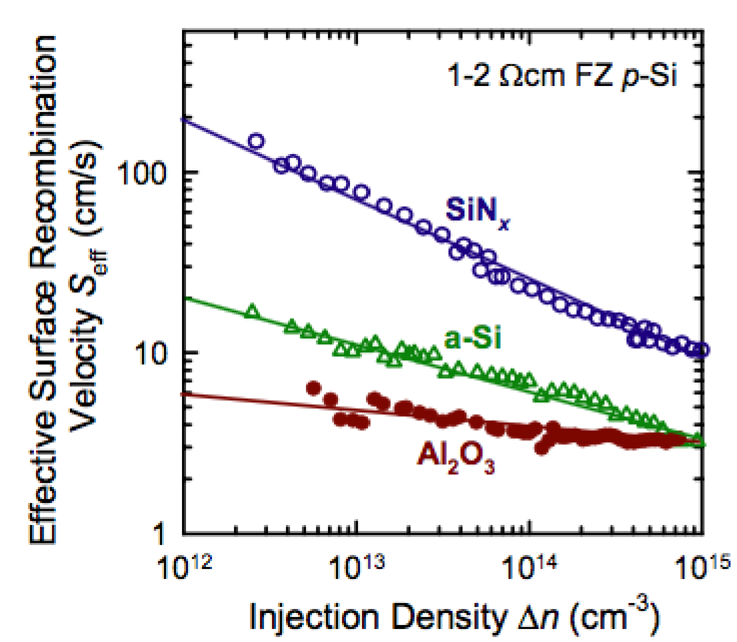
PERT (Passivated Emitter and Rear Totally diffused))

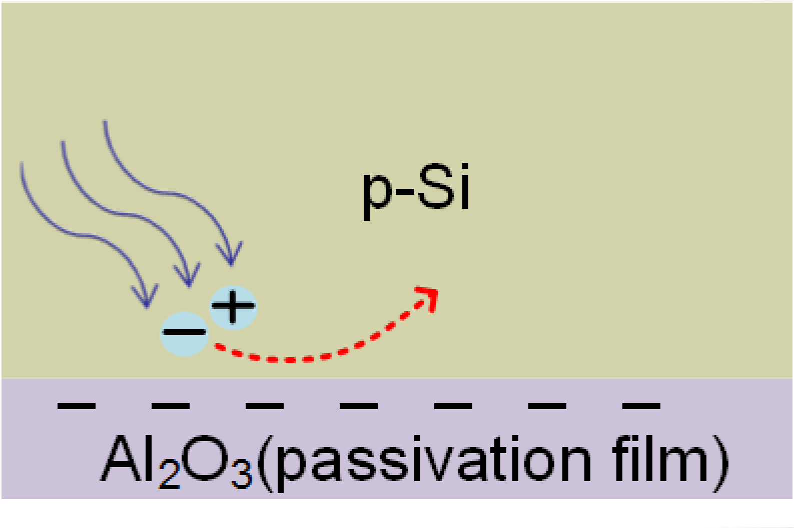
效率能比BSF太陽電池高的關鍵

- **正面利用SiN_x作為n-Si的passivation(有些BSF也如此)**
- **背面利用Al_2O_3等dielectric作為p-Si的passivation**

Ref.: www.photonicsonline.com/doc/how-to-push-conventional-sided-contacted-solar-cells-to-the-max-0001

Passivation (dielectric) Materials

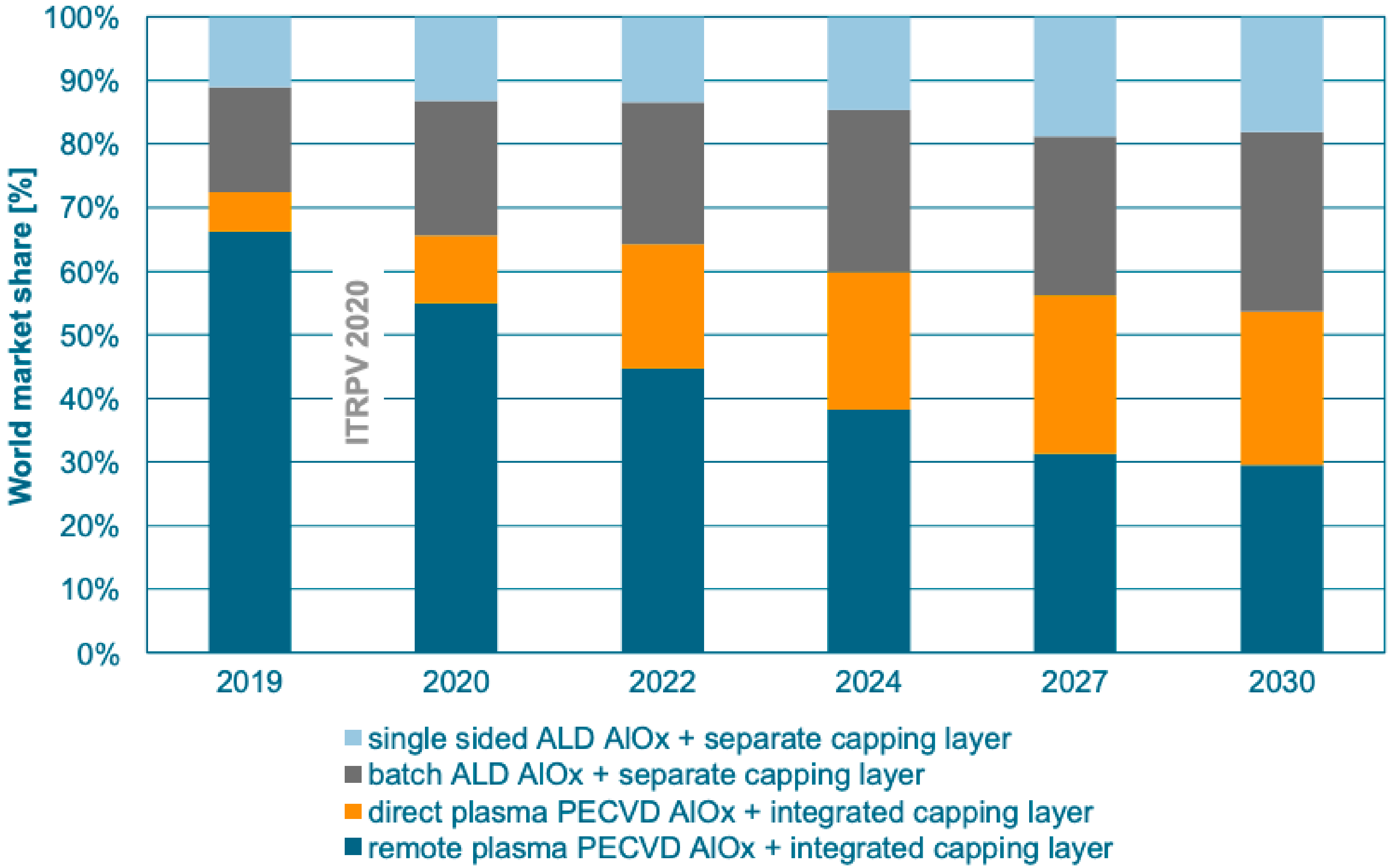




- **a-Si or SiO_2: 漸少表面斷鍵(dangling bonds)，減少復合site**
- **SiN_x(+) or Al_2O_3(-) or GO(-): 藉由薄膜層內的固定電荷來提供場效鈍化(field effect passivation)**

Ref.: Jan Schmidt, EU PVSEC 2008

Different rear side passivation technologies

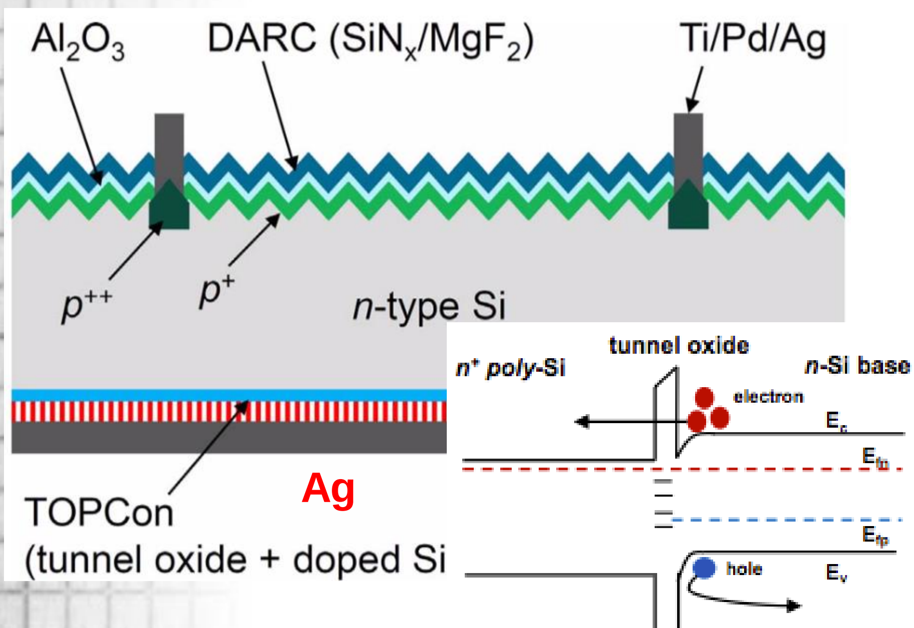


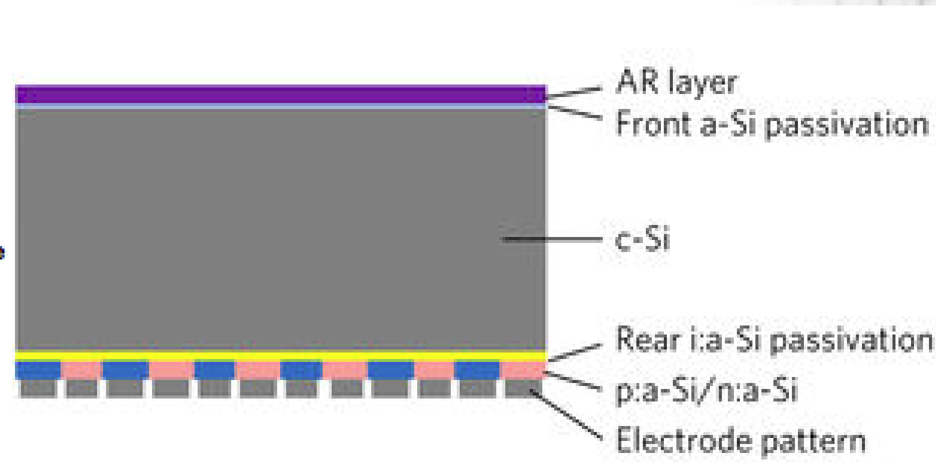
Ref.: ITRPV

New Passivation Technology

Tunnel Oxide Passivated Contact (TOPCon)

Heterojunctions (HJ)+ interdigitated back contact (IBC)





- 有oxide鈍化因而能達25.7 %.
- 不像PERx仍有部分金屬接觸處無法鈍化，n^+Si/n-Si所成的carrier-selective passivating contact 整個面都允許多數載子(e) 通過而阻止少數載子(h)往該方向傳輸。

結合下兩結構優點達26.7 %目前紀錄
- HJ: a-Si layer passivates the c-Si surface
- IBC: 表面無電極阻擋入射光

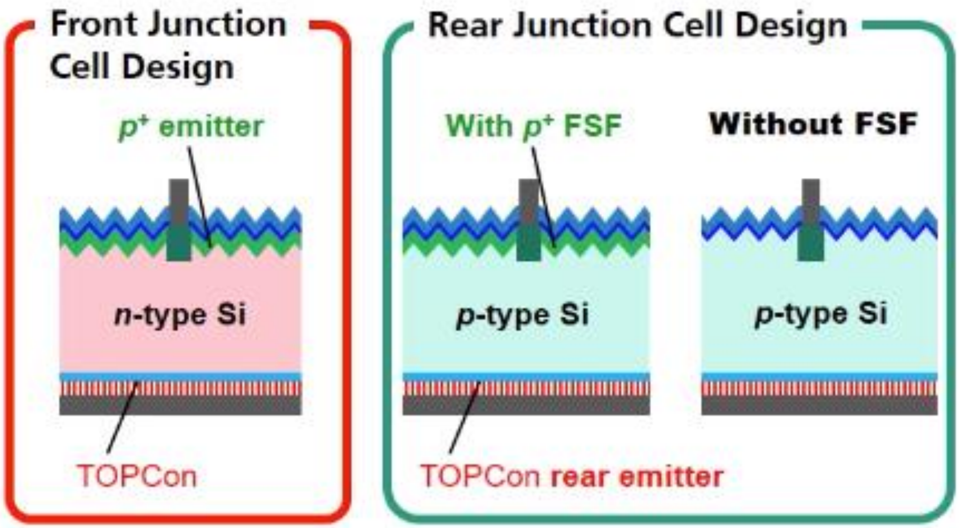
Ref.: S. W. Glunz, SEMSC, 2017
K. Yashikawa et al., Nature energy 2017.

TOPCon再進化

n-Si基座缺點:

•照光所產生的電洞需要藉由p^+ emitter傳導，摻雜太低導電差；摻雜太高則高復合

Ref.: A. Richter (Fraunhofer Institute for Solar Energy Systems (ISE), *Silicon PV 2020*



Design	V_{oc} (mV)	*FF* (%)	J_{sc} (mA/cm²)	η (%)
Front junction [1,2]	724	83.1	42.9	25.8
Rear junction without FSF [3]	**732**	**84.3**	**42.1**	**26.0**

改成p-Si基座:

•背部就由TOPCon協助電子傳導(似pn接面)，已有整面Ag無須橫向傳導(不怕電子傳輸差)

•正面整塊都是p型，電洞傳輸也不太需要靠高摻雜的FSF (front surface field)

•TOPCon潛力:

BSF、PERx升級成TOPCon改裝少、成本少，比起HJT從頭來過好

•TOPCon挑戰:

要解決鍍poly-Si時繞鍍到正面，多流程造成之成本與穩定度問題

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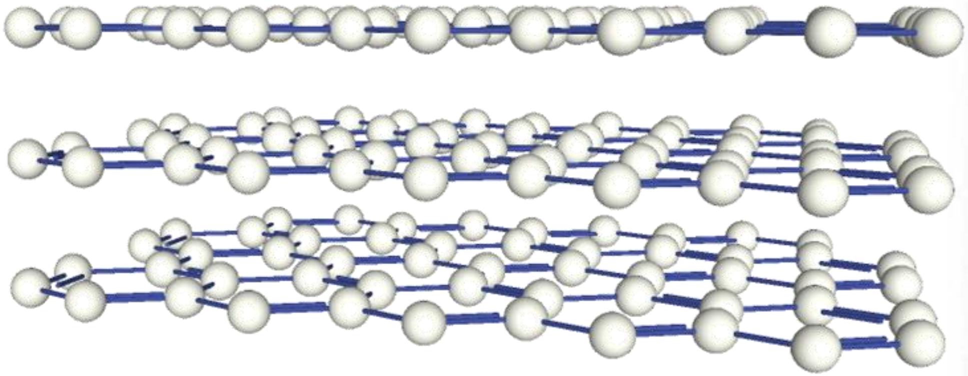
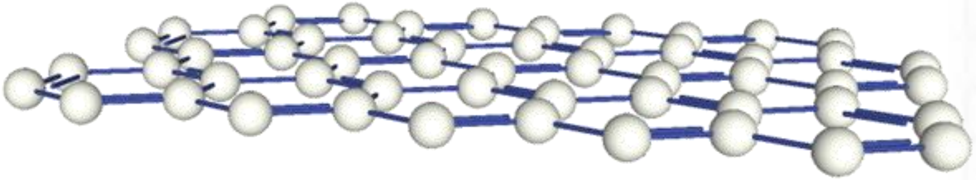
Graphene vs. Graphene Oxide

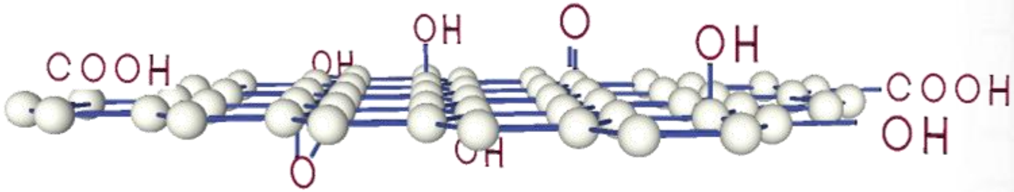
- Graphite



- Graphene

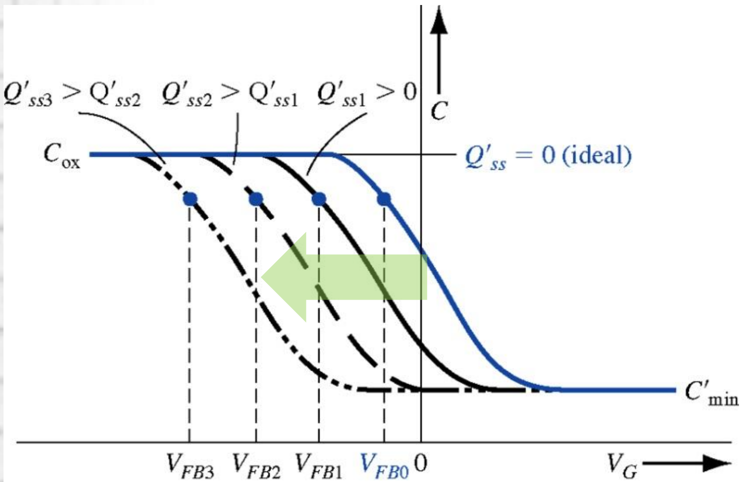


- Graphene Oxide(GO，氧化石墨烯)



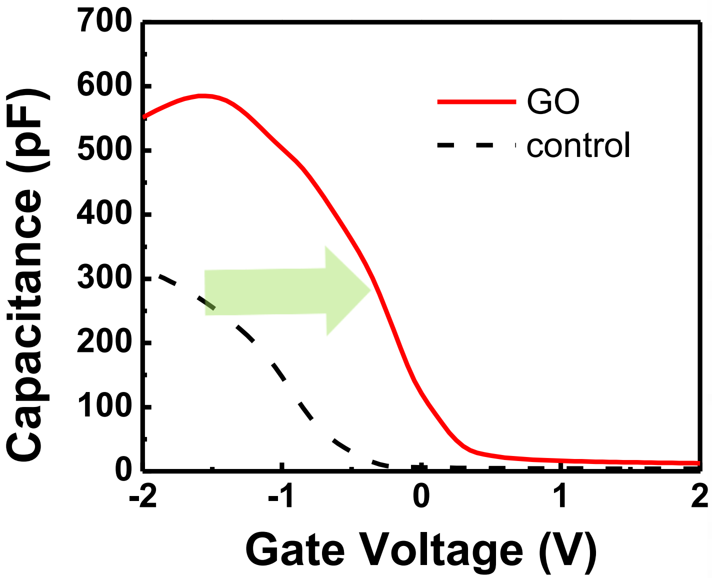
Our Finding: Negative Charge in GO

- From textbook,
we know :
w/ positive charge



$$V_{FB} = \phi_{ms} - \frac{Q'_{ss}}{C_{ox}}$$

- w/ negative charge

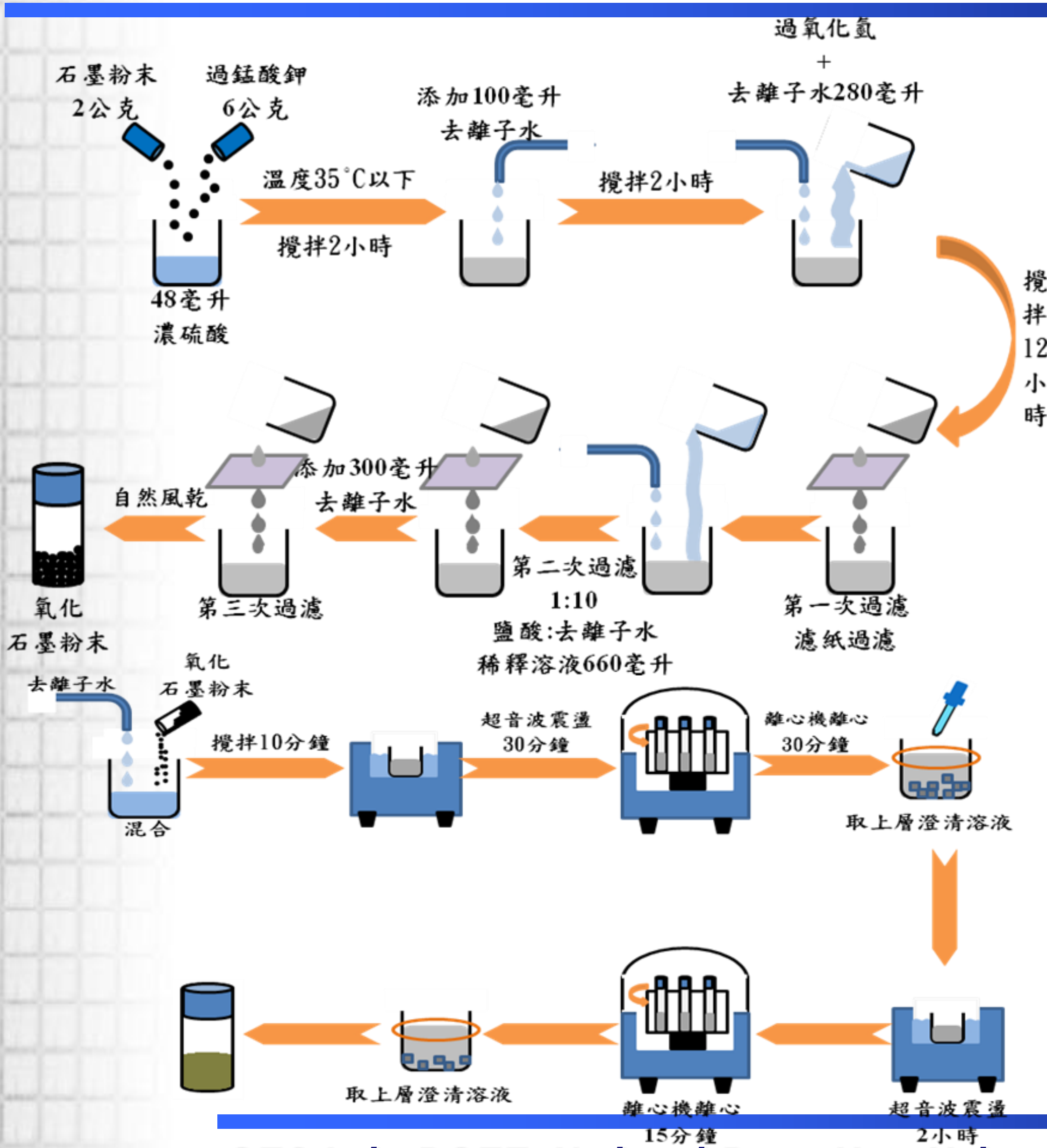


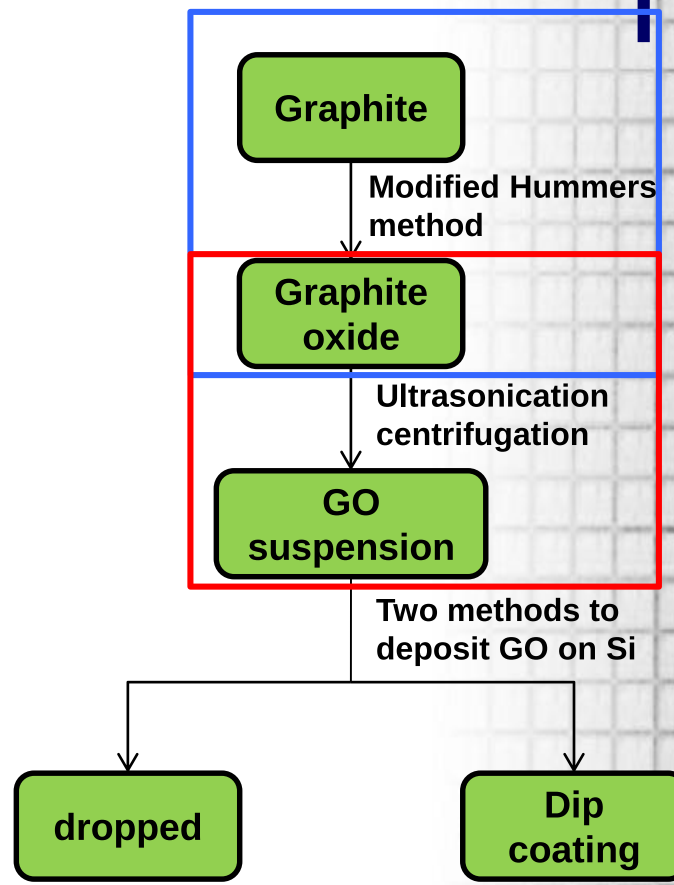
- Charge density: $-6\text{x}10^{12}$ /cm^2
- Other common used materials:

Al_2O_3: $-3\text{x}10^{12}$ /cm^2

SiN_x: 10^{12} /cm^2

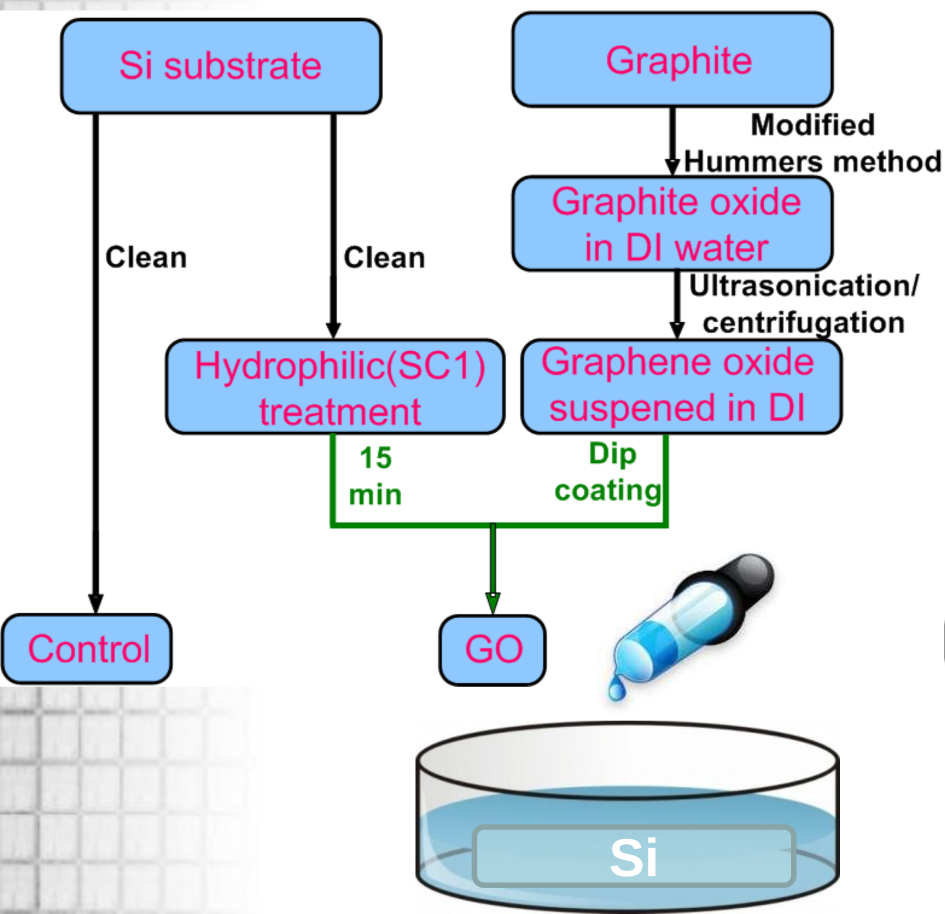
Our procedure to prepare GO film



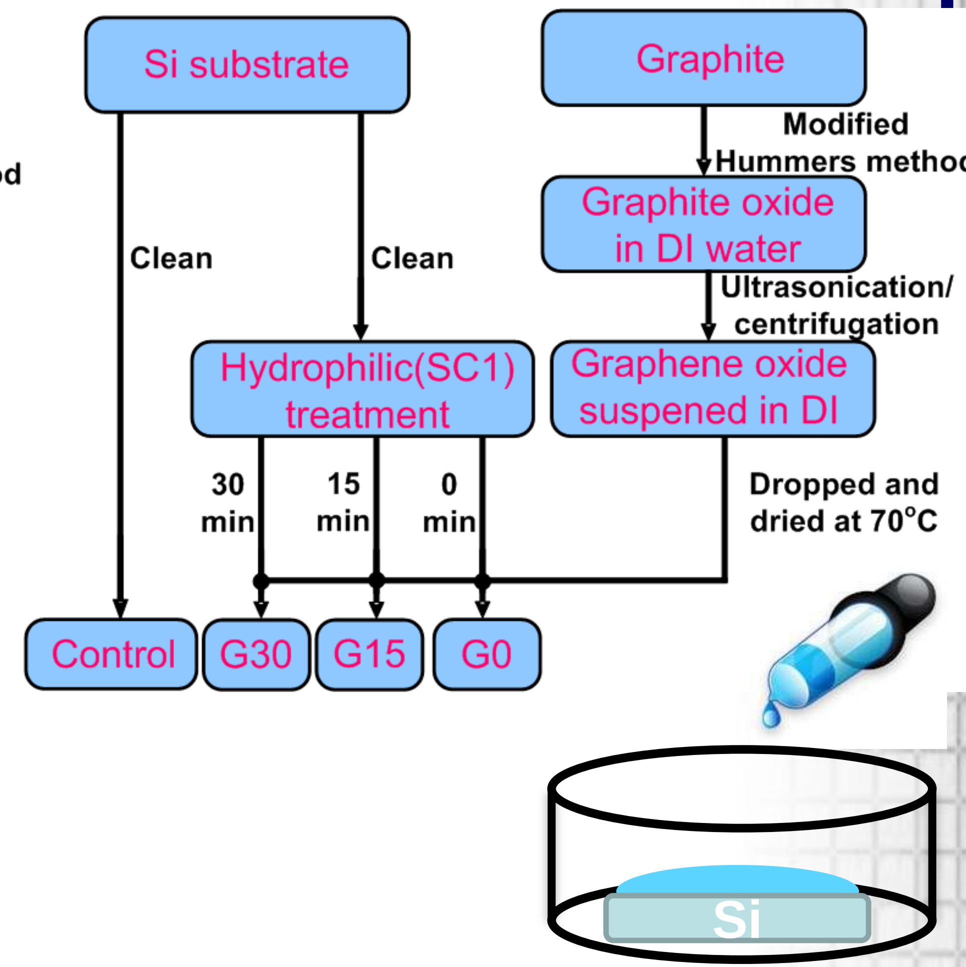


Ways to deposit GO film

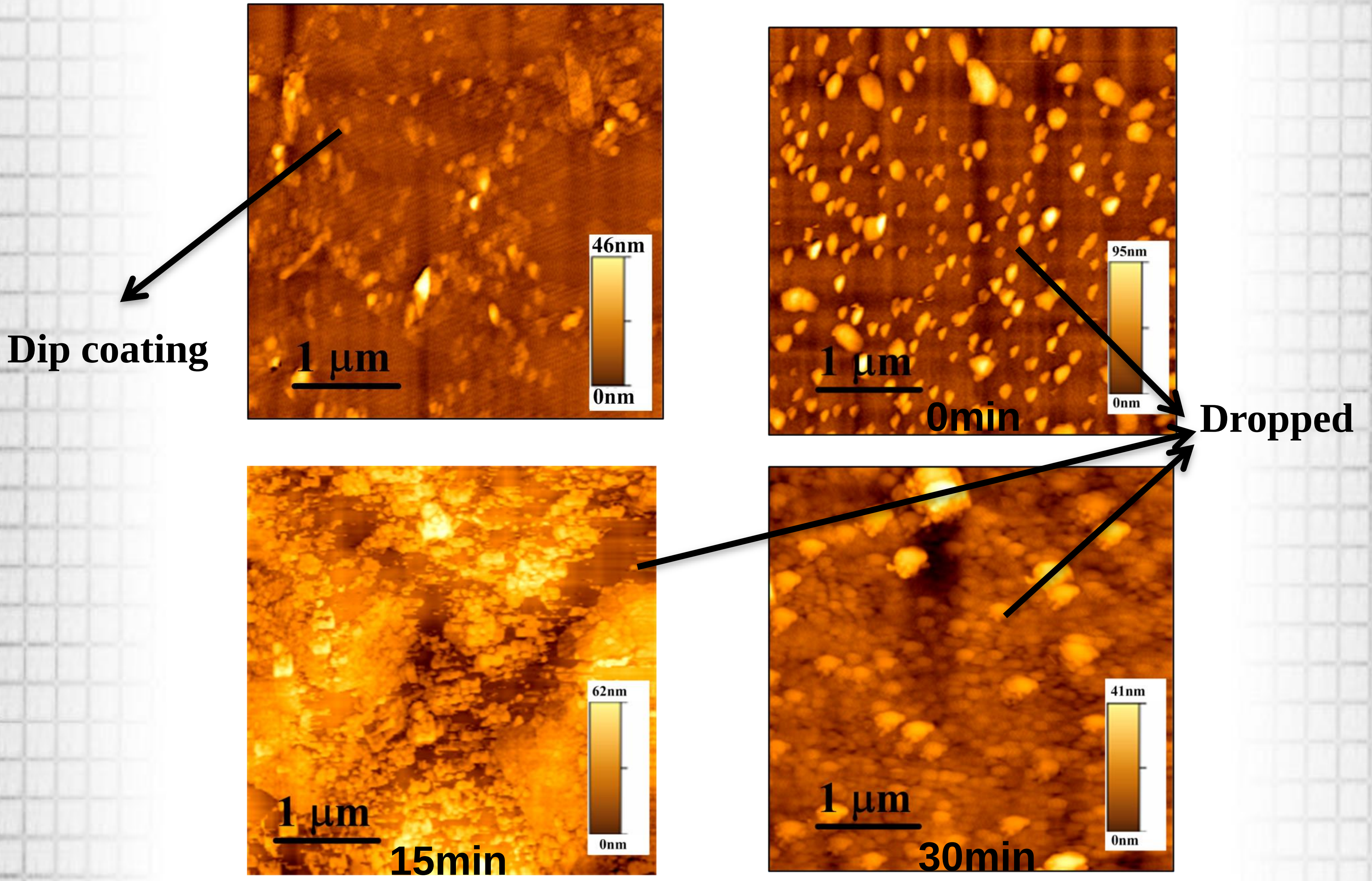
Dip coating ：



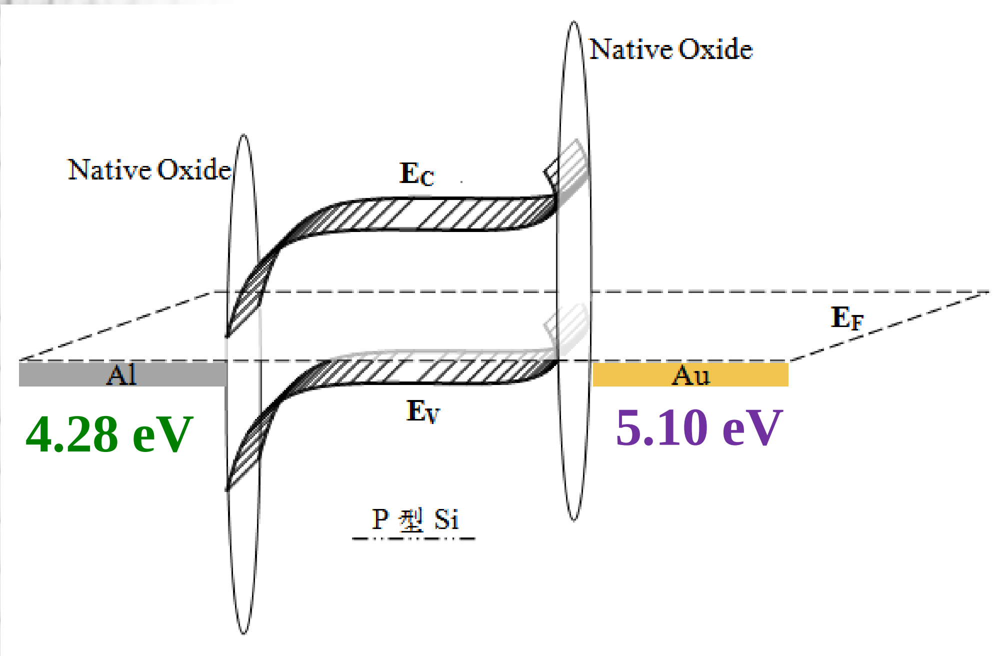
Dropped ：

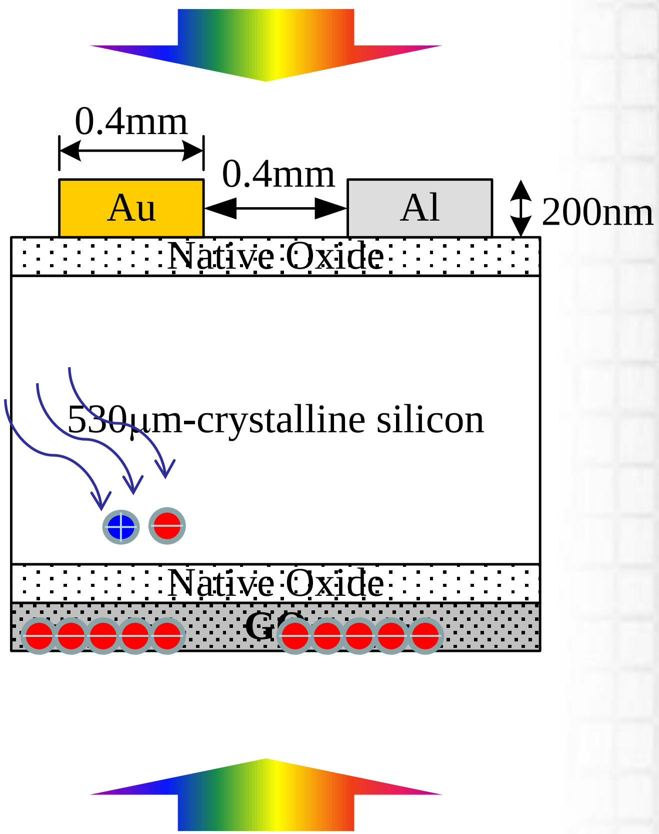


表面形貌 by Atomic Force Microscope(AFM)



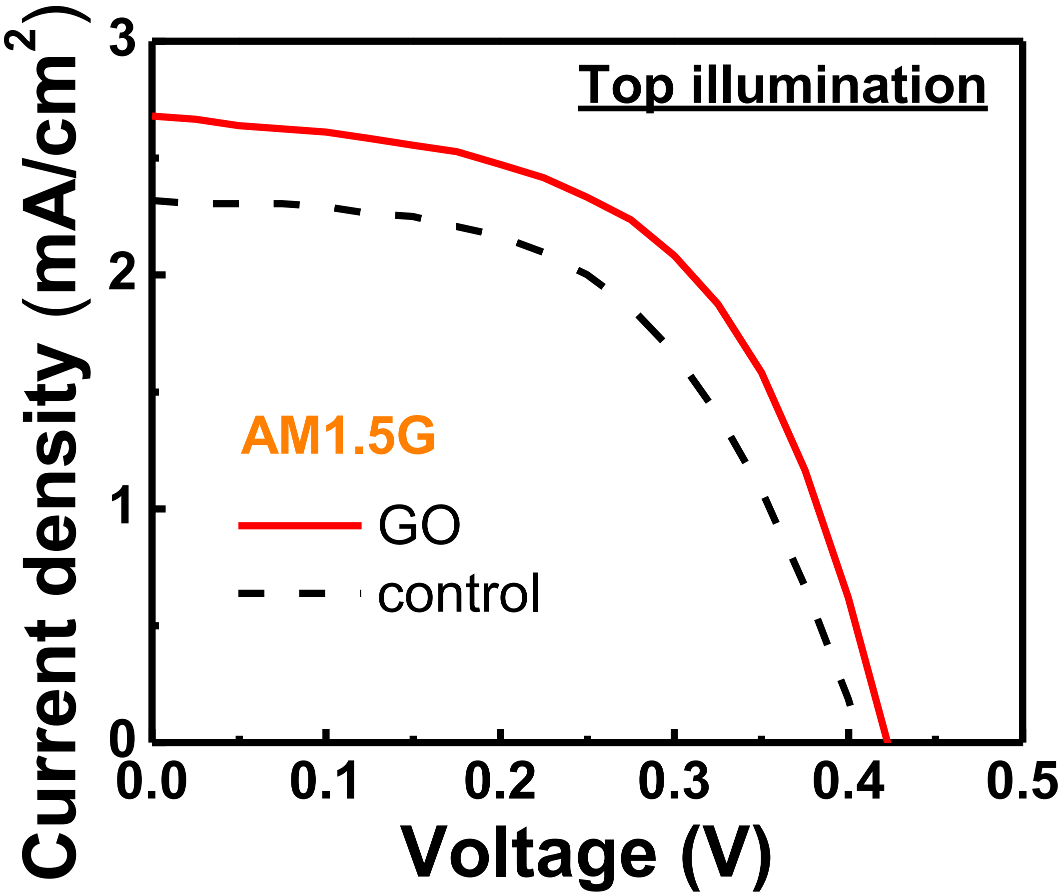
Two-metal Cell Passivation by GO



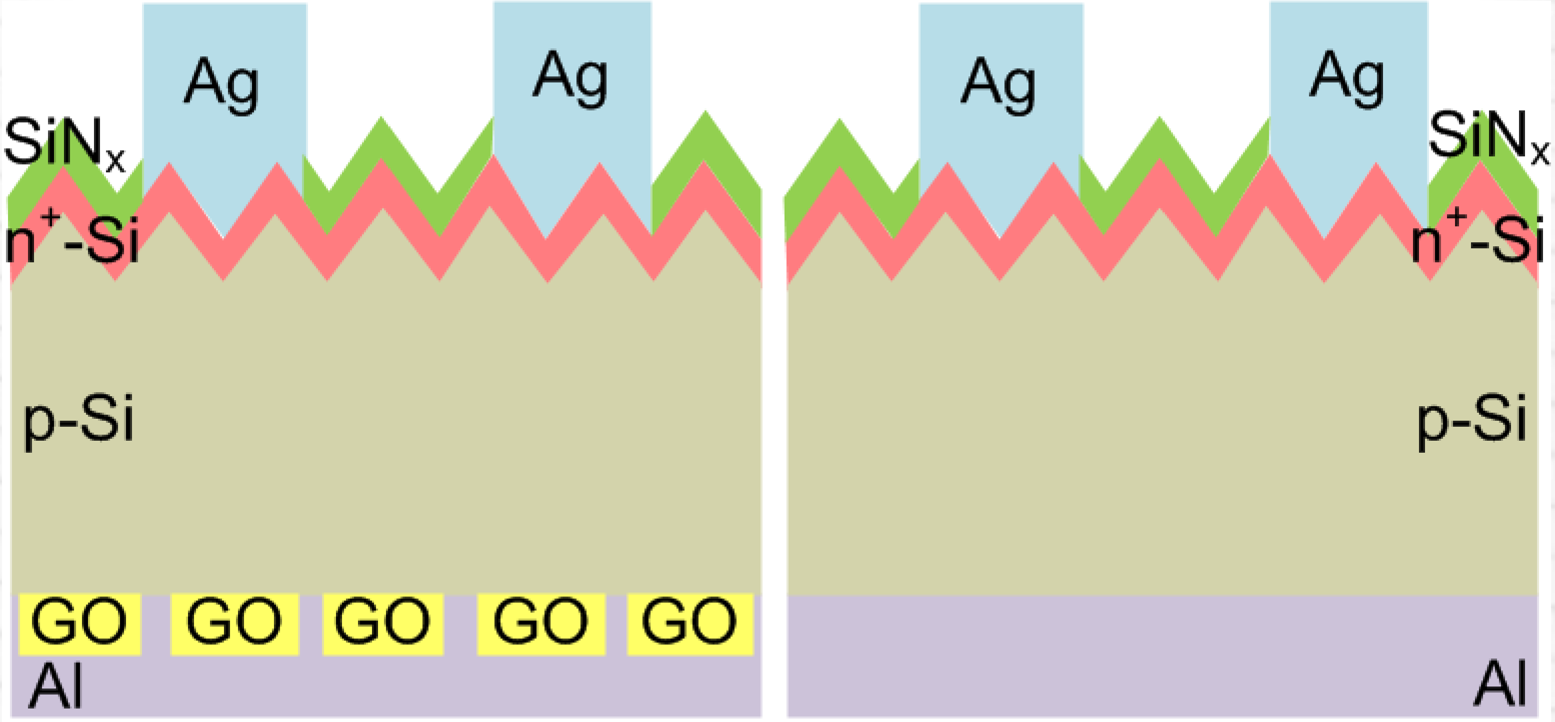


GO 確實能提升Two-Metal Cell之表現

•GO introduction contributes to 21 % enhancement on the efficiency.
•But only from 0.52 to 0.63 %



Demonstration on Si pn-junction Cells



(a) GO (b) control

- 為了說明我們的GO有用於業界鈍化的價值

=>得在商用pn太陽電池上展現GO也能提升效率

=>下一頁我們比較在p-Si背面是否有蓋GO鈍化層的電池表現

I-V Characteristic Improvement

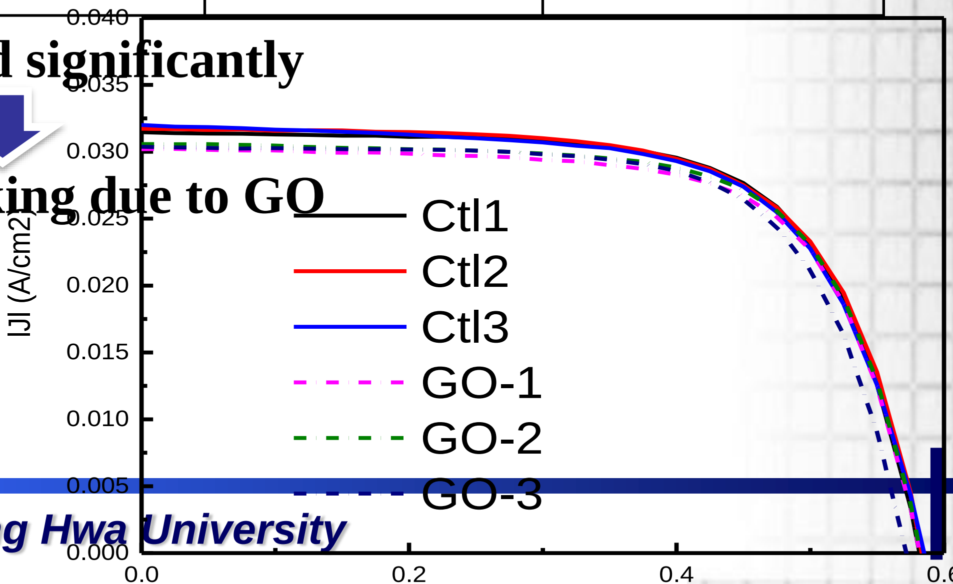
	V_{oc}(V)	J_{sc}(mA/cm²)	FF	η(%)
Ctl1	0.582	31.46	0.75	12.45
Ctl2	0.583	31.72	0.74	12.38
Ctl3	0.585	32	0.73	12.33
GO-1	0.582	30.19	0.76	12.02
GO-2	0.583	30.58	0.76	12.23
GO-3	0.572	30.37	0.75	11.89

J_{sc} decreased significantly

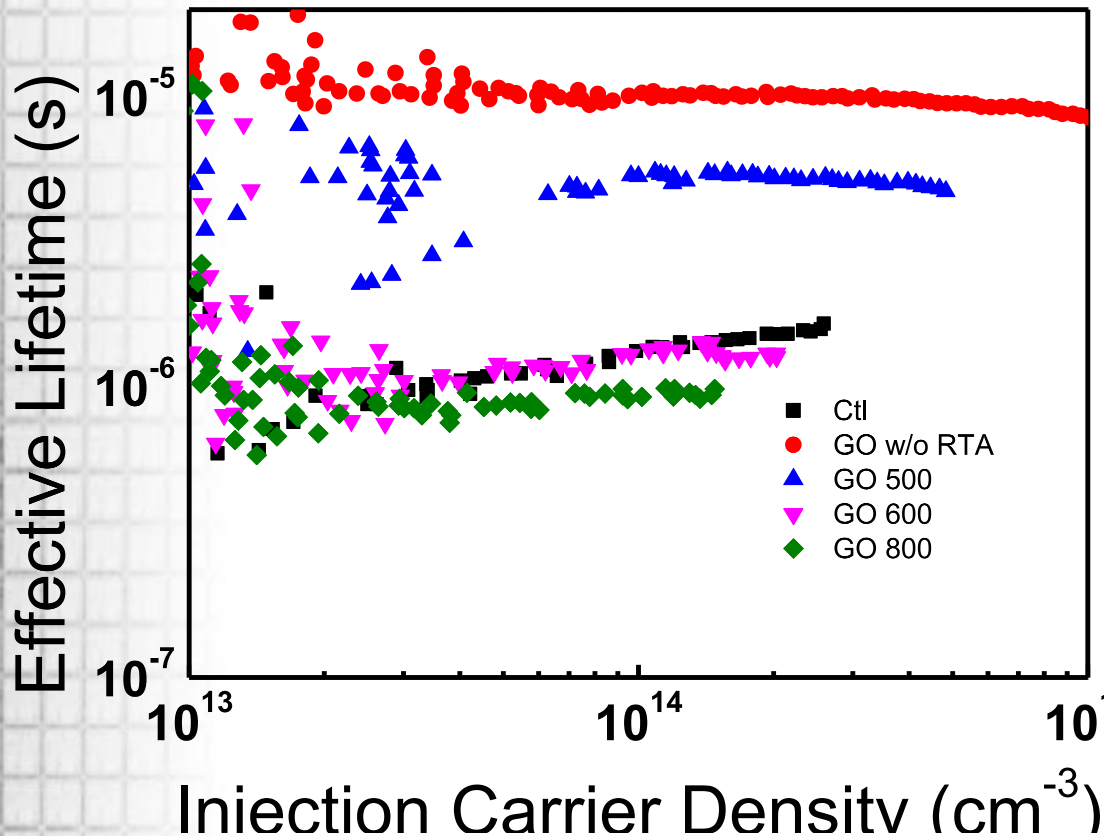
Current blocking due to GO

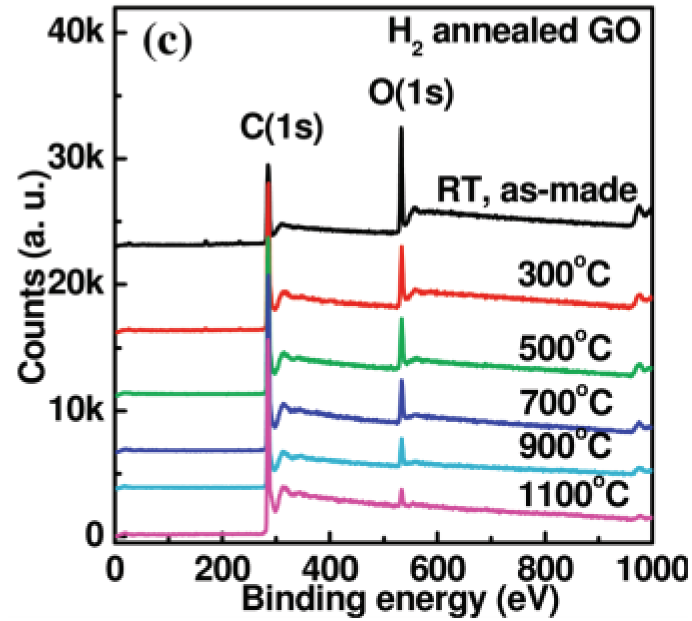
No V_{oc} enhancement

No passivation effects?



高溫製程會消磨掉GO所提升的載子壽命





- Ref. J. AM. CHEM. SOC. 2009, 131, 15939
- O peak decreases as T increasing
- Passivation due to GO (fixed charge) may degrade.

•網印的燒結參數:

4 s to 400°C (keep 1 min)

7 s to peak T (800 for ex) (keep 4s)

•上圖說明了商用太陽電池中網印的高溫製程，衰退了太陽電池中的載子壽命(lifetime)

UNSW最近也發表了GO鈍化研究，但仍未用於電池

Lifetime接近1ms τ_{eff} (μs)

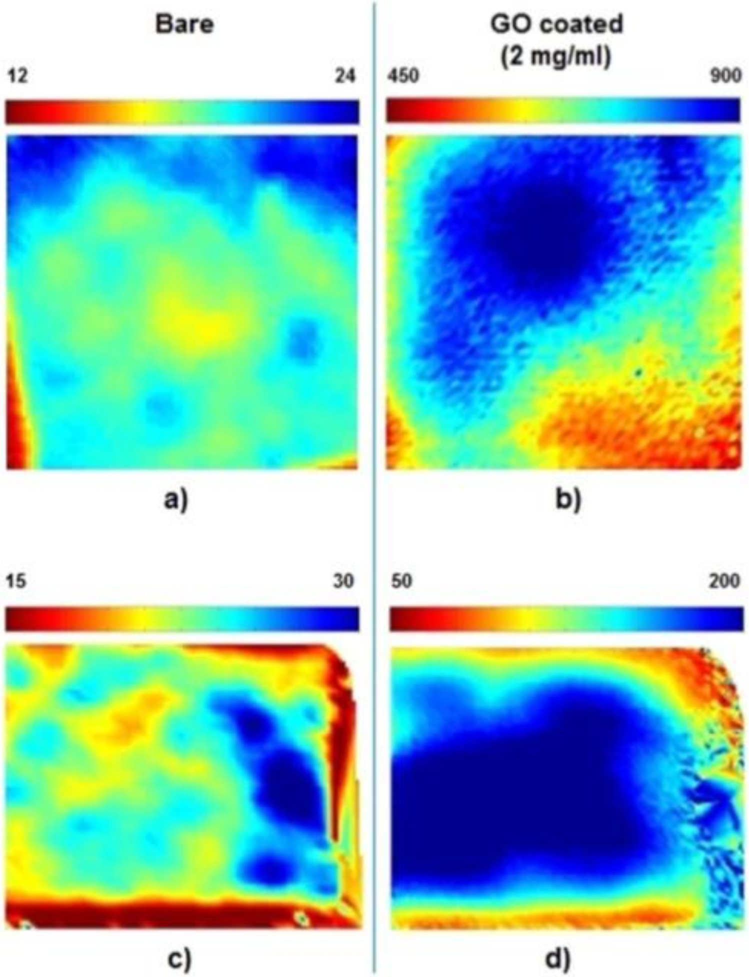


Fig. 1. Effective lifetime maps of a DSP FZ p-type (> 1000 Ω·cm) silicon sample (a) bare and (b) GO coated, and a SSP Cz p-type (2.8 Ω·cm) silicon sample (c) bare and GO coated.

XPS確認GO確有負電荷引起表面空乏

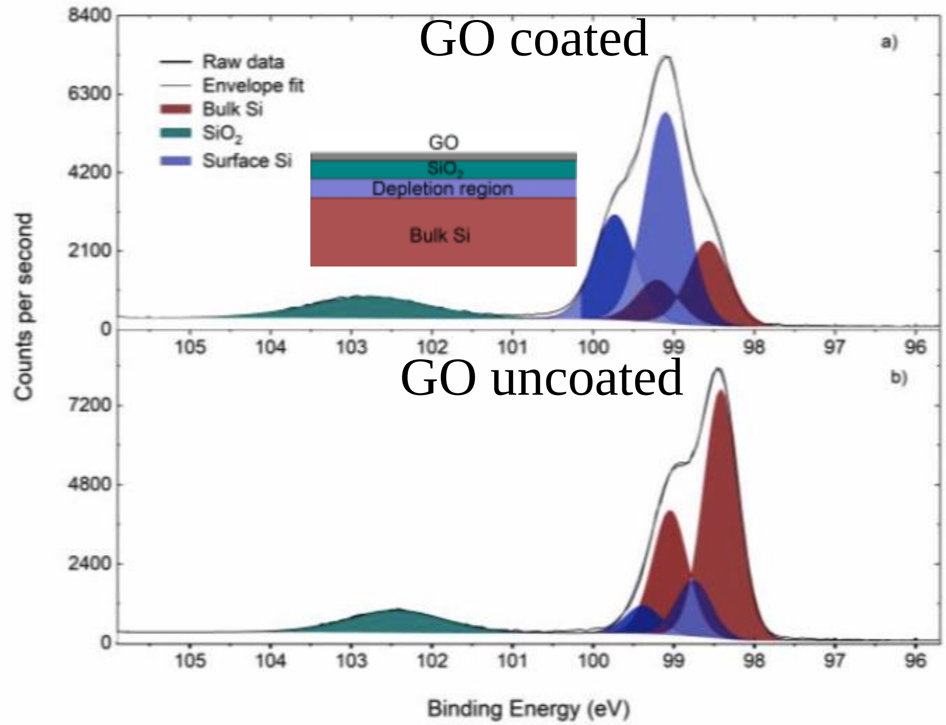
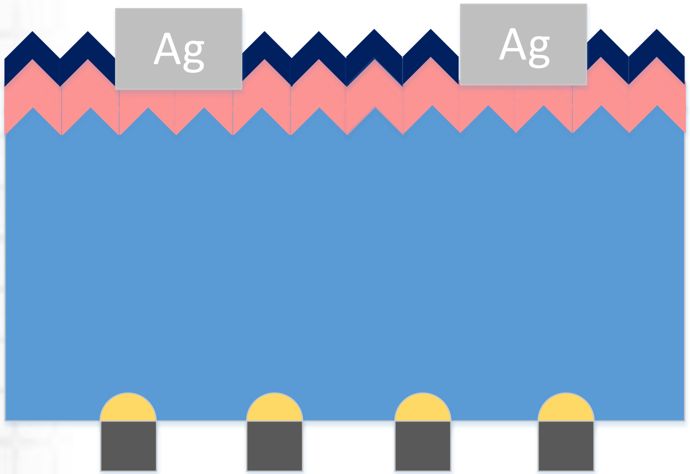


Fig. 3. Si 2p spectra of (a) GO coated Si/SiO_2 sample and (b) uncoated Si/SiO_2 sample showing a shift from the oxide peak on the coated sample and the shift and splitting of the Si $2p_{3/2,1/2}$ peak.

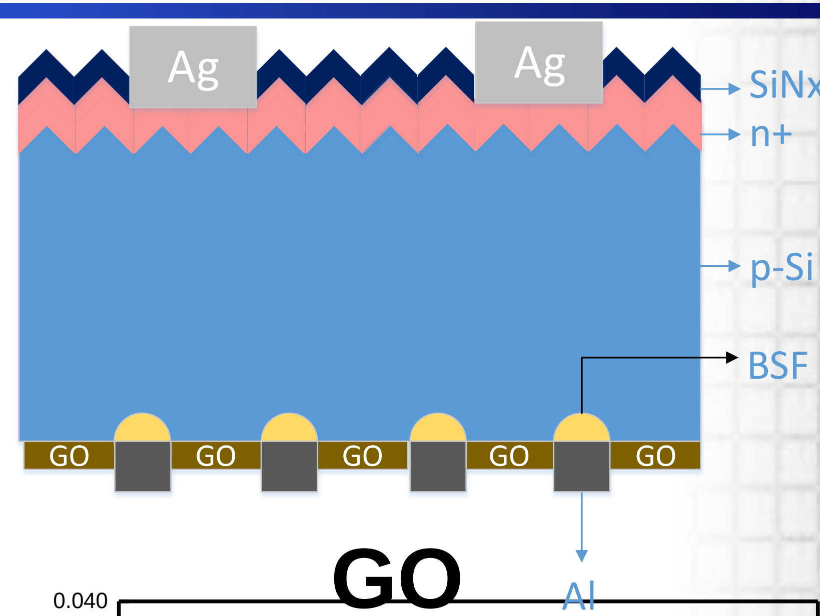
Ref: University of Manchester, *SEMSC*, 2018
University of New South Wales, *PVSC* 2019

Solar Cell w/o High T process

Bifacial Structure

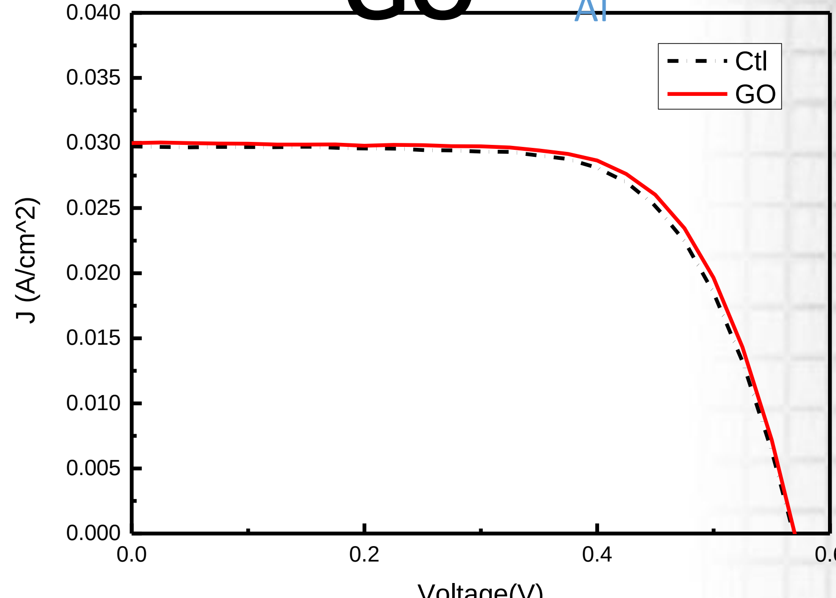


Ctl

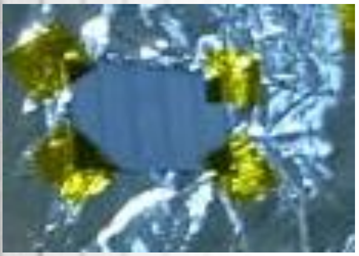


GO

	Voc(V)	Jsc(mA)	FF	η(%)
Ctl	0.568	29.73	0.73	11.47
GO	0.570	29.99	0.75	11.74

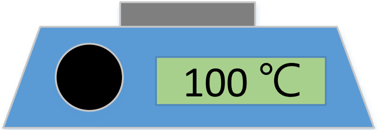


Experimental Process II for Bifacial Structure

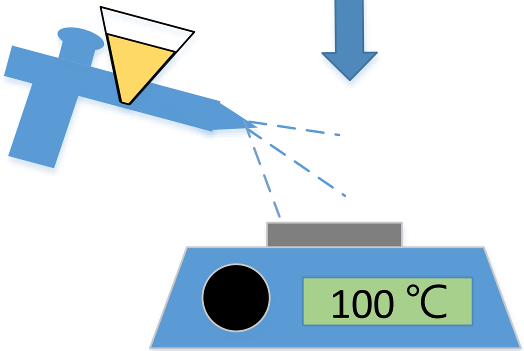


Taking something cover busbar

Drop GO into spray gun



Preheat to 100 degrees

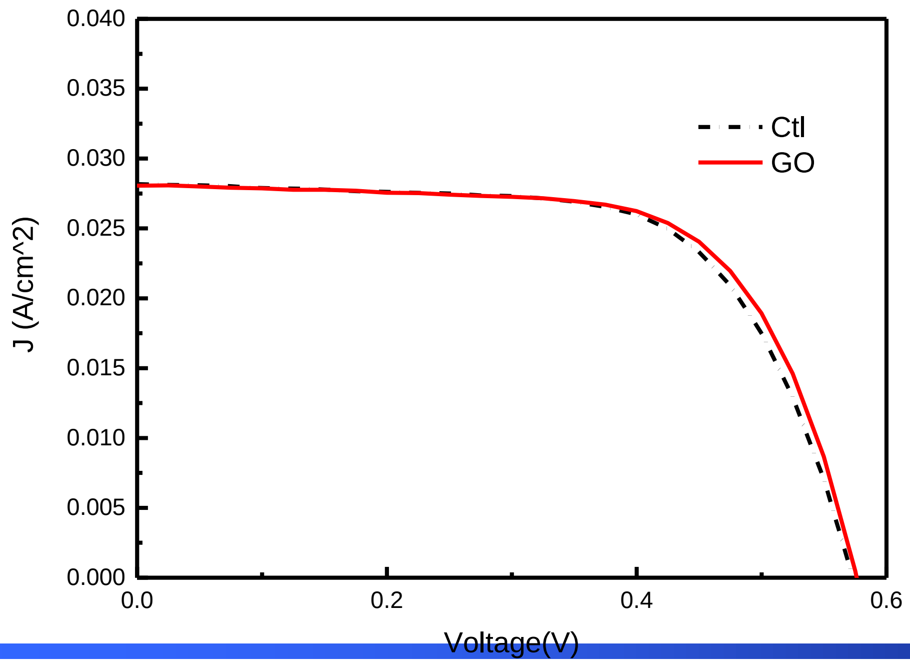


Use a spray gun in an appropriate way so that the sprayed liquid can evaporate immediately

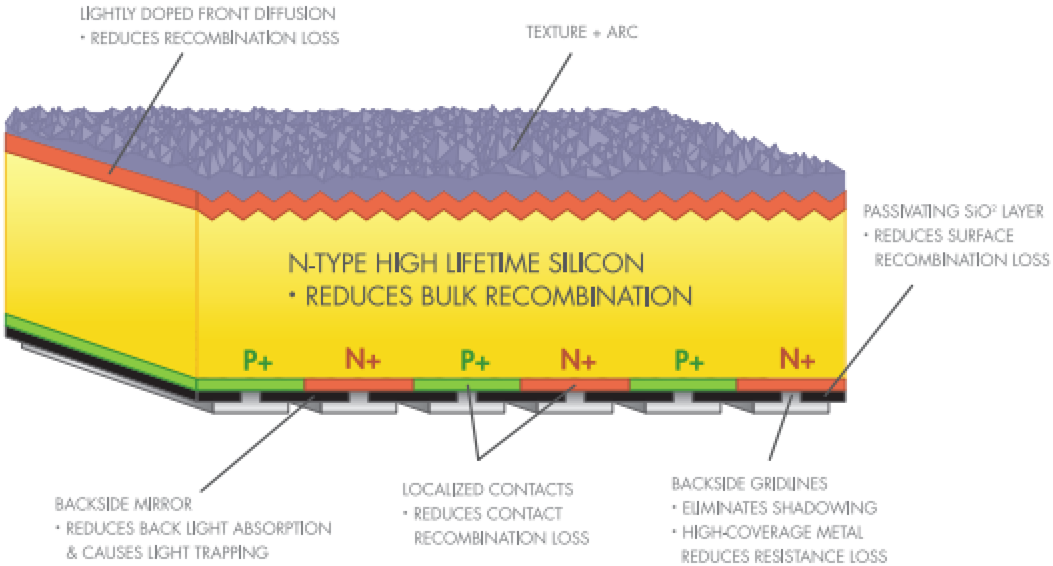
Spray until the liquid is exhausted

Results from Bifacial Structure II

	Voc(V)	Jsc(mA)	FF	η(%)
Ctl	0.573	28.17	0.72	10.61
GO	0.576	28.06	0.73	10.82



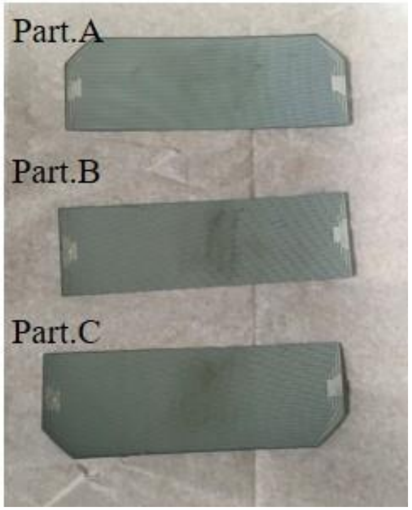
GO on Interdigitated back contact (IBC)

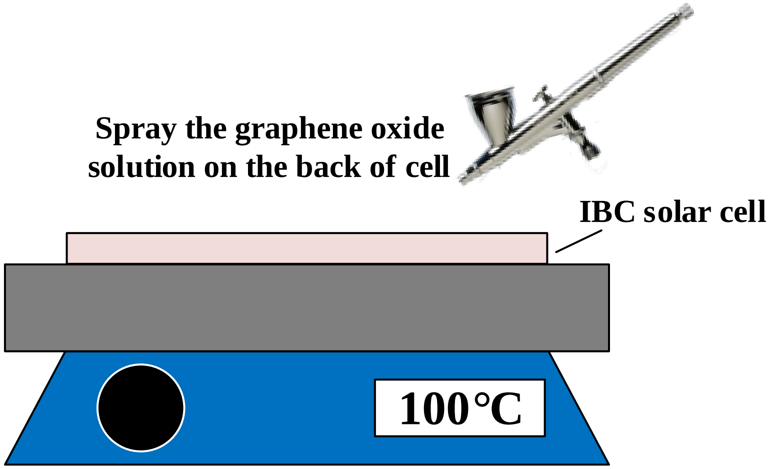


Back GO Passivation within electrodes

Ref. https://us.sunpower.com/sites/sunpower/files/media-library/brochures/br-sunpower-solar-panels-are-most-efficient-solar-panels-pv-industry.pdf

IBC電池上GO前後的電池表現

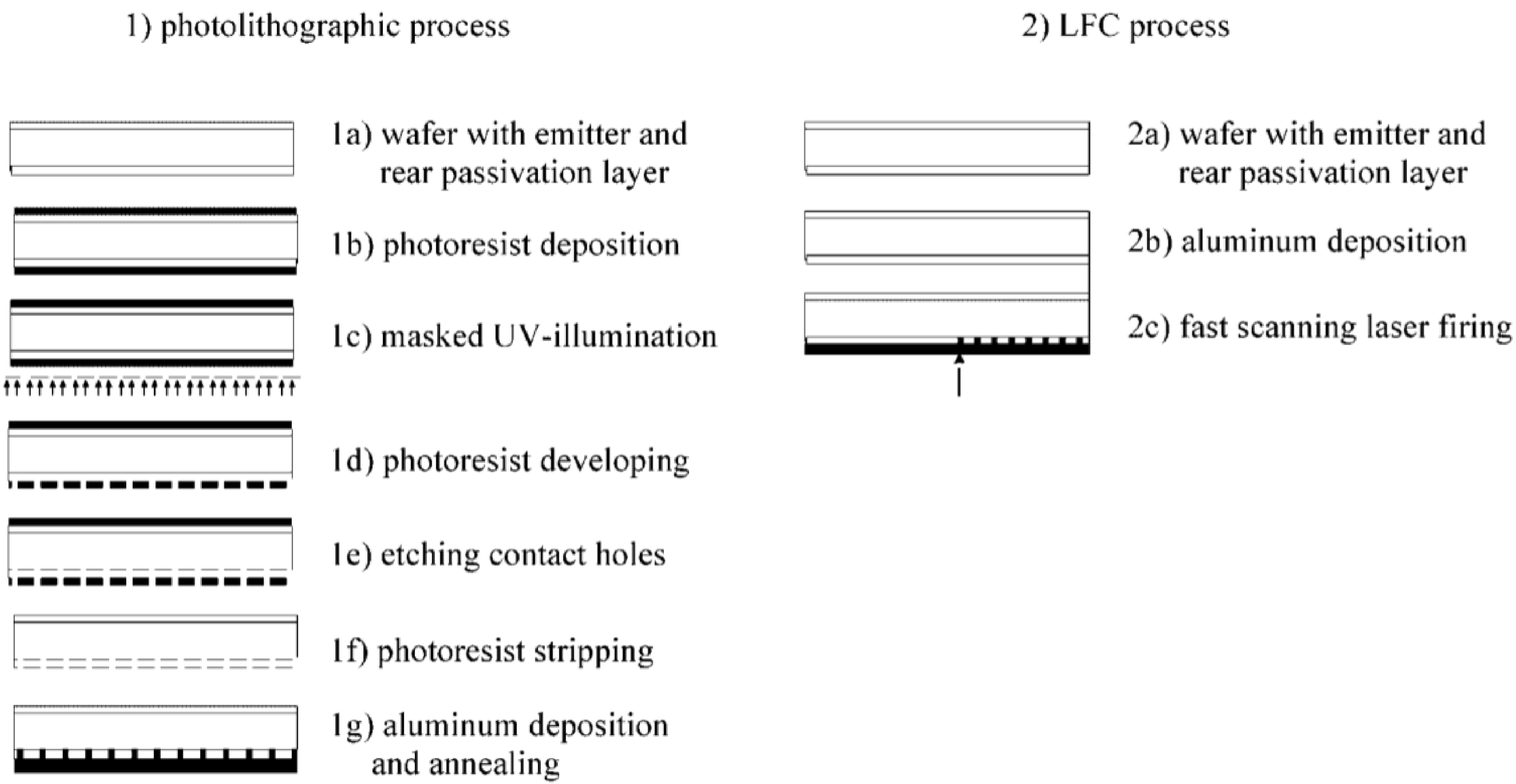




上GO前	Illuminated area(cm^2)	Voc(V)	Isc(mA)	FF	η(%)
Part.A	28.6	0.625	0.857	0.72	13.42
Part.B	24.7	0.622	0.753	0.67	12.63
Part.C	28.6	0.631	0.870	0.74	14.17

上GO後	Illuminated area(cm^2)	Voc(V)	Isc(mA)	FF	η(%)
Part.A	28.6	0.631	0.904	0.72	14.28
Part.B	24.7	0.627	0.909	0.66	13.48
Part.C	28.6	0.635	0.909	0.77	15.62

Laser-fired Contacts (LFC)局部加熱

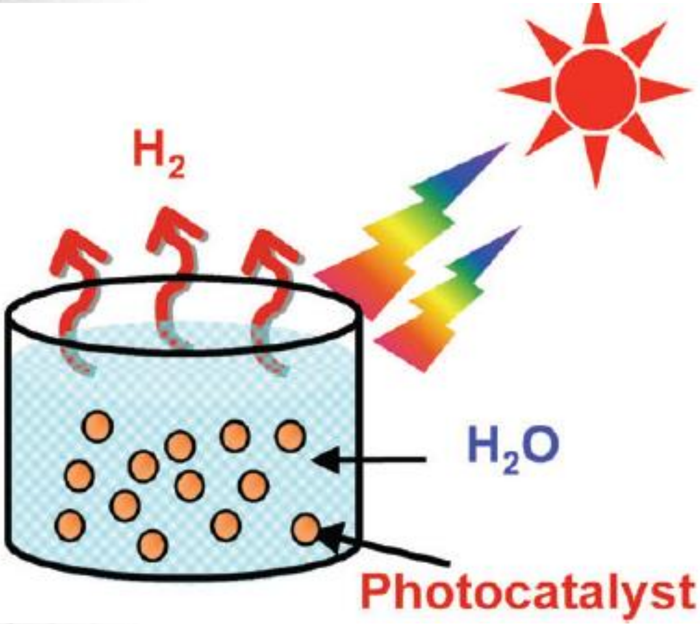


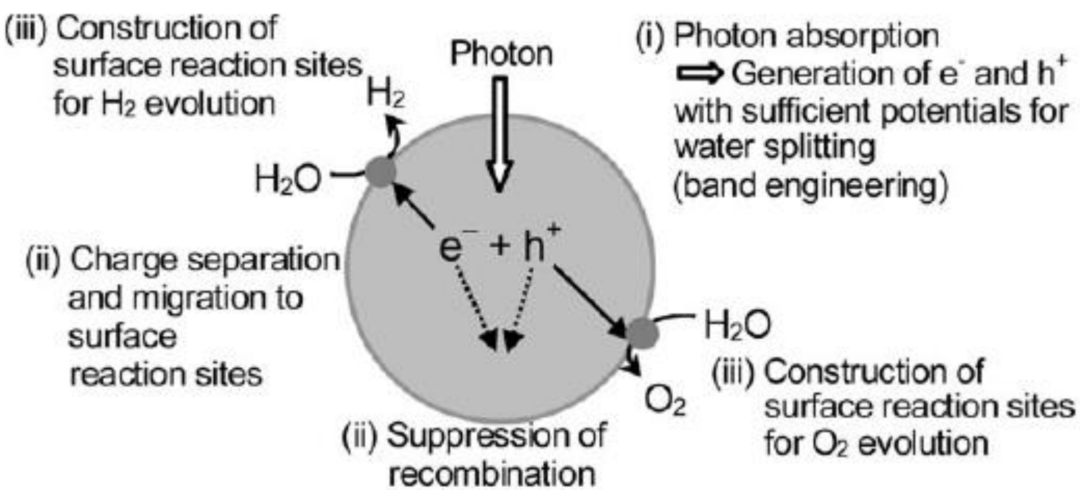
Ref. Prog. Photovolt: Res. Appl. 2002; 10:29

Outline

- Introduction
- Passivation Technologies
- GO for Solar Cell Passivation
- GO for Solar Water Splitting
- Summary

水分解產氫



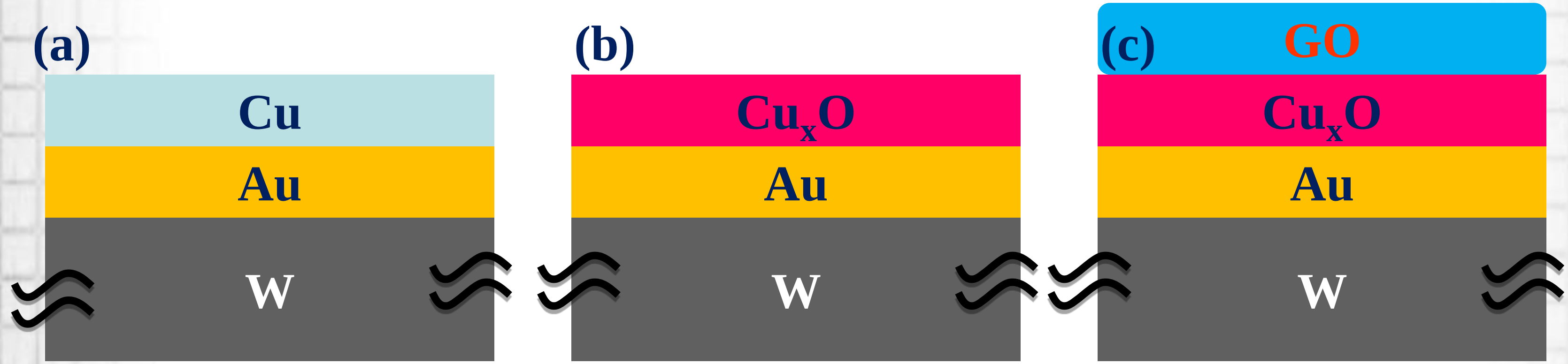


•在(半導體)光觸媒的幫忙下，可利用太陽能分解水產出H_2及O_2而不需要外加偏壓或犧牲試劑

•H_2 能用於燃料電池，其燃燒放能只排放出水(H_2O)，為潔淨能源

Ref. Chem. Soc. Rev., 2009, 38, 253–278

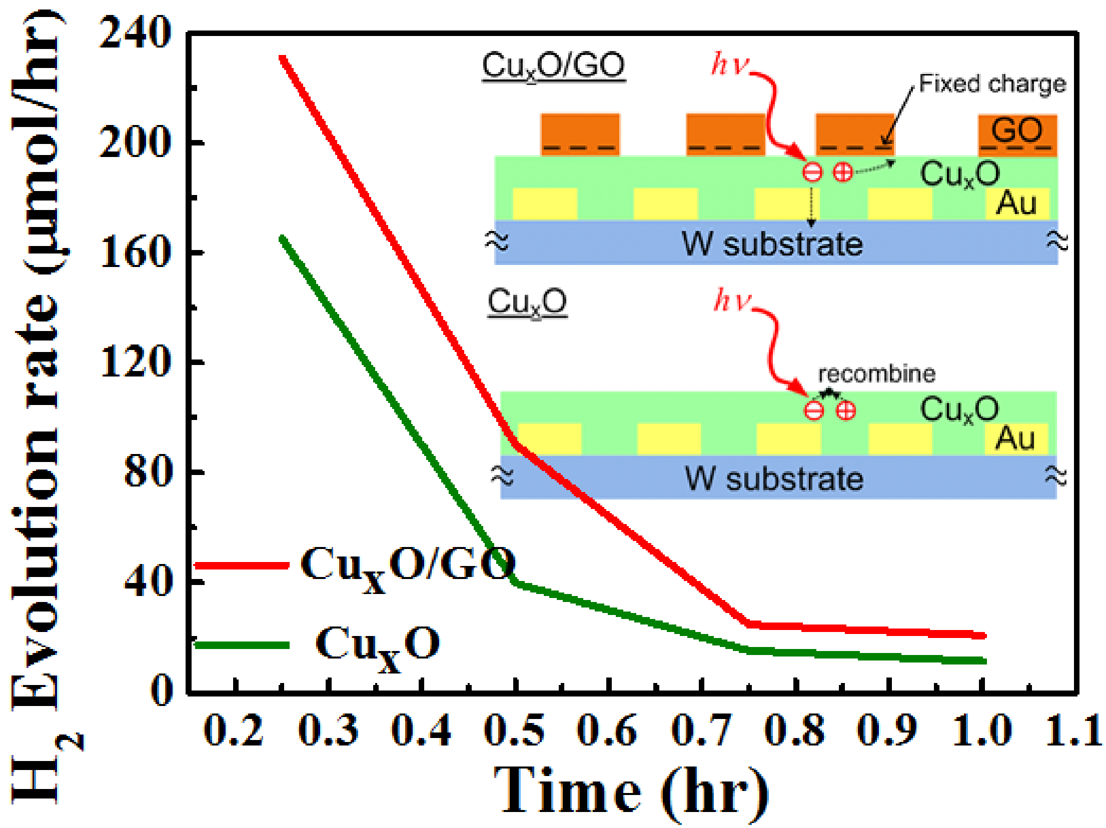
Device Structure



Metal deposition　　Cu oxidation at 190 ℃　　Precipitation of GO

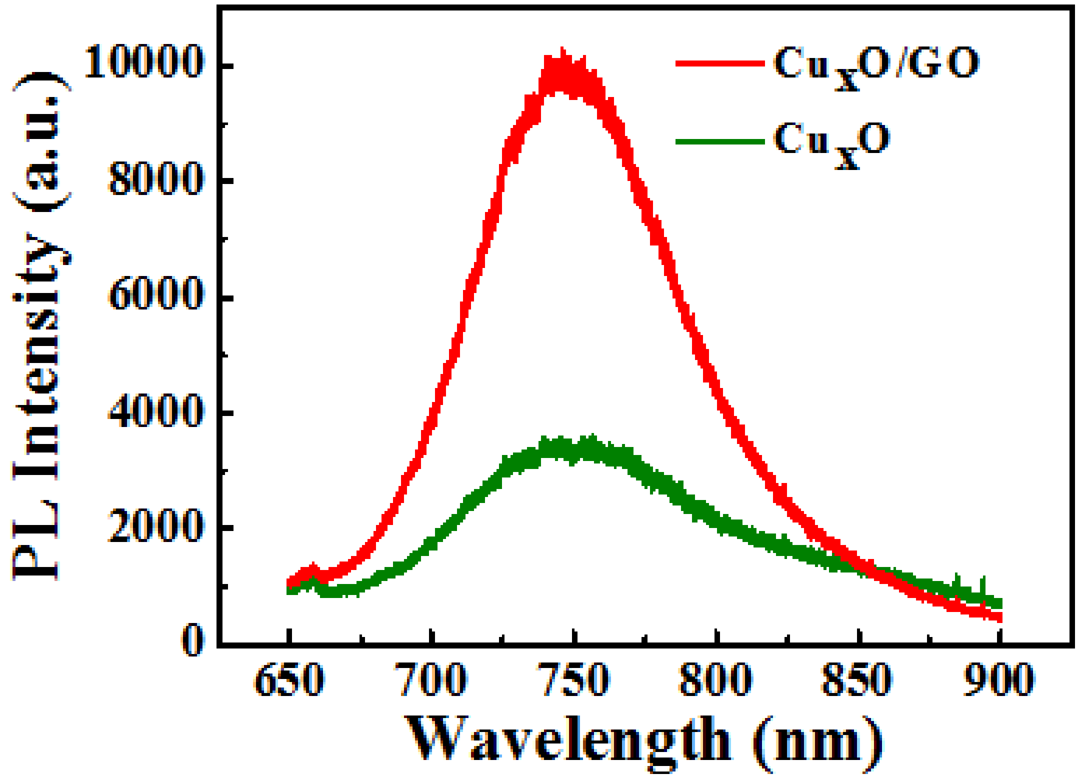
- W 提供良好導電率(相較於矽)
- Au and Cu: each 20 nm
- 在空氣中以190℃ 加熱10 hr以將Cu氧化

產氫速率



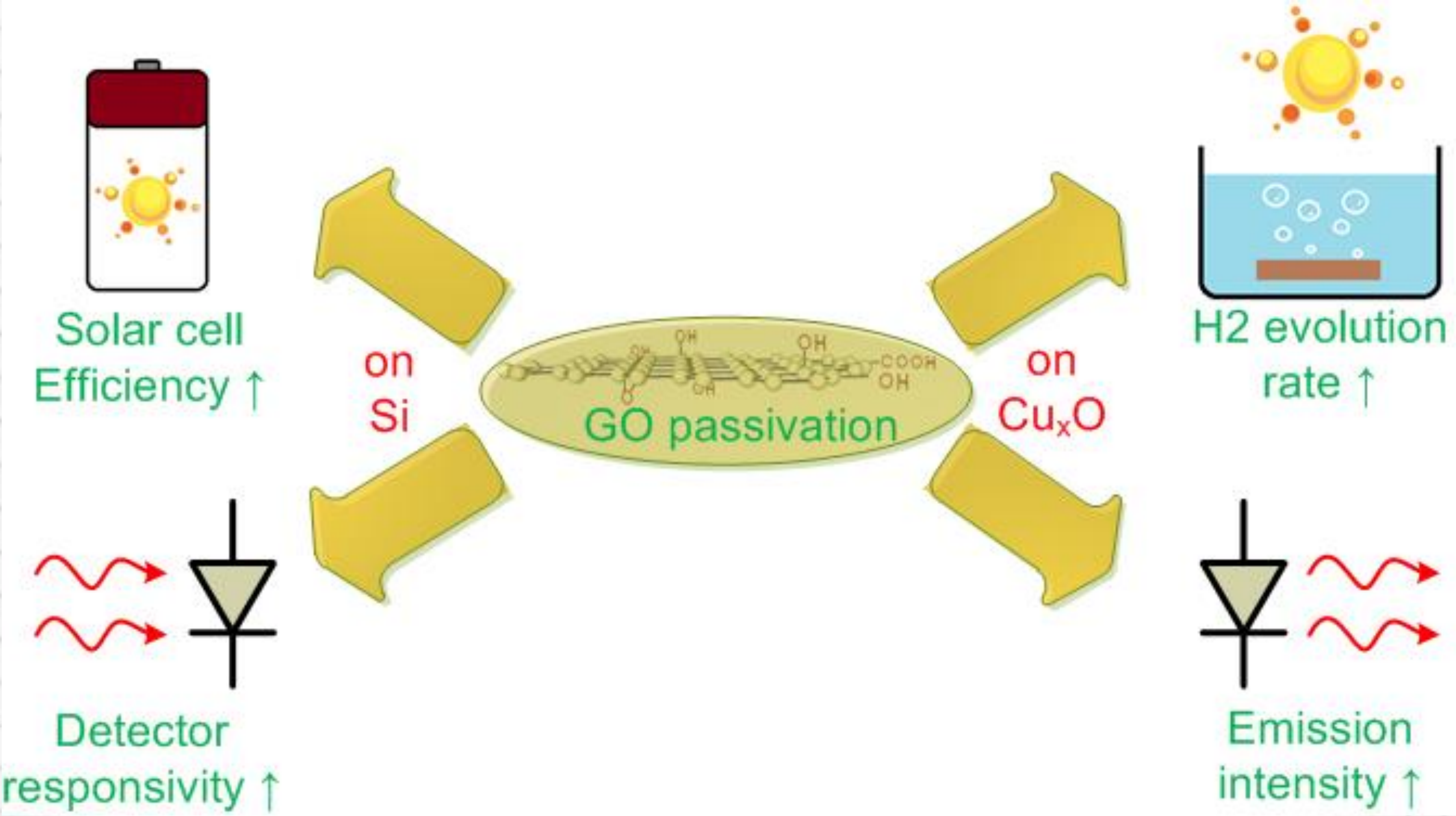
- Cu_xO/GO及Cu_xO 樣品一開始的產氫速率分別是230及170 μmol/hr
- 多蓋一層GO，產氫速率提升35 %，原理如插圖，一樣是passivation貢獻

GO增強PL 強度



- 以632 nm (w/ energy < Eg of GO)雷射照射樣品，觀測在Cu_xO中電子電洞對復合放出的光
- 一樣可藉由GO的鈍化，減少了電子電洞對在表面的熱復合(因而有更多機會改藉由放光復合)

Summary


Solar cell
Efficiency ↑
on
Si
GO passivation
on
Cu_xO
H2 evolution
rate ↑
Detector
responsivity ↑
Emission
intensity ↑

Summary

- 矽電池發展多年，要將效率往上繼續提升，仰賴好的鈍化技術。無論是PER_x背部的Al_2O_3、HJT的a-Si、IBC正面SiN_x與背面SiO_2都是為鈍化而存在。

- 鈍化可以抑制光生電子電洞對的復合，提高載子的lifetime，進而提升太陽電池效率。

- 若能將氧化石墨烯(GO)用於無須高溫的製程，有機會利用其化學塗佈方式，降低鈍化的成本。

Thank you for your attention!