薄膜太陽能電池研討會
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Industrial Technology
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新材料微晶矽鍺薄膜太陽電池

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2010/11/15 PM3:00～5:40
台大博理館 101演講廳

Outline

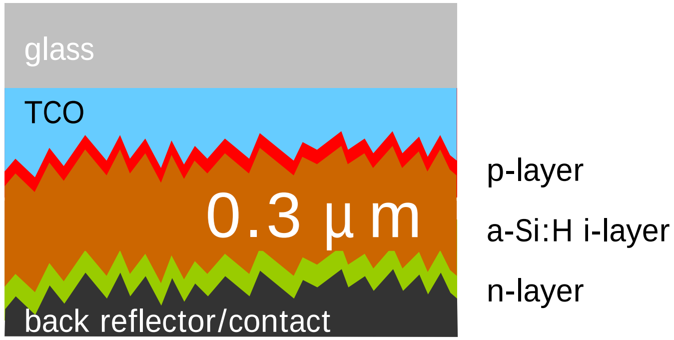
- Introduction
- Conventional thin film silicon solar cell
  - Challenges in a-Si:H and a-Si:H/μc-Si solar cell
- A new concept of thin film μc-$Si_{1-x}Ge_x$:H solar cell
  - Advantages and opportunities
  - Challenges
- Properties of μc-$Si_{1-x}Ge_x$:H thin film
  - ESR spin densities (neutral dangling bonds)
  - Carrier densities
- Conclusions

Si thin film

Si bulk-type

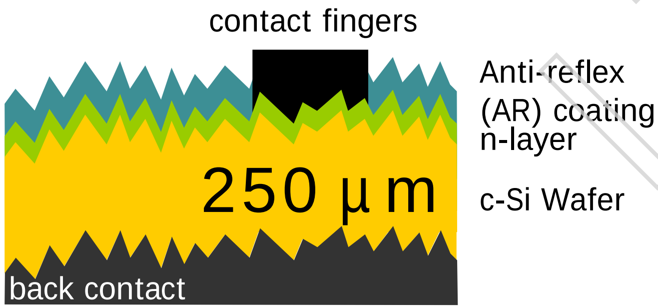
Why Silicon Thin Film for Solar Cells?

Thin Film



1000 x thicker

Wafer



Silicon Thin Film Technology:

- low material consumption 0.3 µm to 3 µm
- established large area
- deposition techniques (Flat Panel Industry)
- low process temperatures (< 300ºC)
- low-cost substrates (glass, plastics, metal, stainless)
- higher energy yield
- low energy pay back time

Silicon-based as raw material:

- abundantly available
- non-toxic & ecologically harmless

Advantages of Si thin film solar cell

Cost Performance → Grid Parity

PV technologies

Category	Technology		Efficiency
Silicon	Mono c-Si		25.0%
	Multi c-Si		20.4%
	Thin film Si		15.4%
Compound semiconductors	Monocrystalline (InGaP, InGaAs, Ge)		35.8%
	Polycrystalline	Cu(In, Ga)Se_2	20%
		CdTe	16.4%
Organic	Thin film (solid)		6.5%
	Dye sensitized		12.3%
Quantum effect	Quantum dot, multi-quantum-well		

Target

日本NEDO計畫電池及模組之性能目標(轉換效率%)

個別技術的開發	太陽電池[1]	現狀		2017年		2025年		2050年
		模組(%)	電池[5](%)	模組(%)	電池[5](%)	模組(%)	電池[5](%)	模組(%)
	結晶矽[2]	~16	25	20	25	25	(30)	40%超高效率太陽電池(追加開發)
	矽薄膜	~11	15	14	18	18	20	
	CIS系	~11	20	18	25	25	25	
	化合物系[3]	~25	41	35	45	40	40	
	染料敏化	-	11	10	15	15	15	
	有機系[4]		5	10	12	15	15	

1) 電池的技術指標以實驗室小面積規格為主。模組則為實用化技術階段。
2) 結晶矽不予以單晶、多晶分類，以使用矽基板之太陽電池為設定。
3) 集光時的轉換效率。
4) 新型太陽電池之有機系太陽電池也為設定之開發目標。
5) 為達成模組目標所設定之電池最低轉換效率。

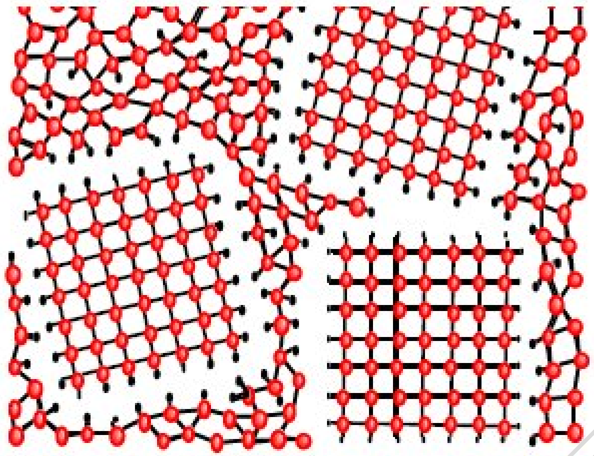
工研院 張佳文翻譯 (2010)

Thin Film competition

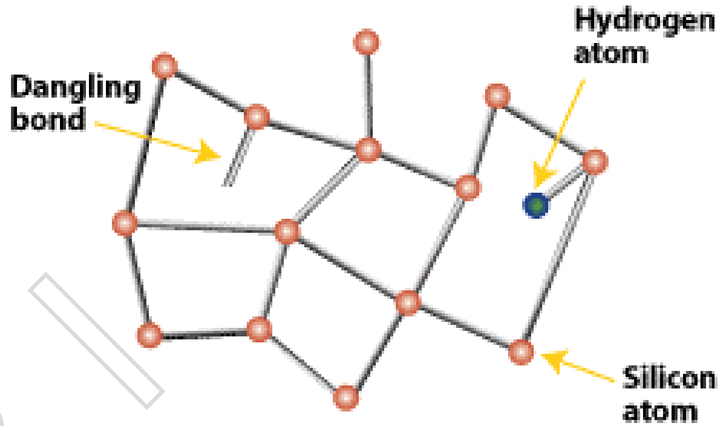
- **Si(Ge)**
  - Abundance, environment safety, ubiquitous
  - Limited efficiency, equipment cost (throughput)
  - Multi-junction
- **CdTe**
  - Low cost, process simply, high throughput
  - Toxicity (Cd), rare element (Te), recycling problem
  - Single junction
- **CIGS**
  - High potential efficiency (~20%), tunable Eg
  - Toxicity (In compound), rare element (In)
  - Single junction

Schematic structure

a-Si:H

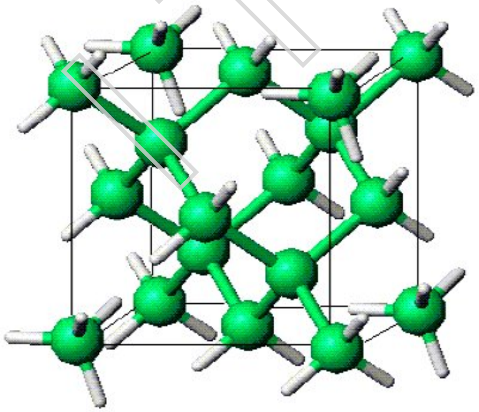


μc-Si:H

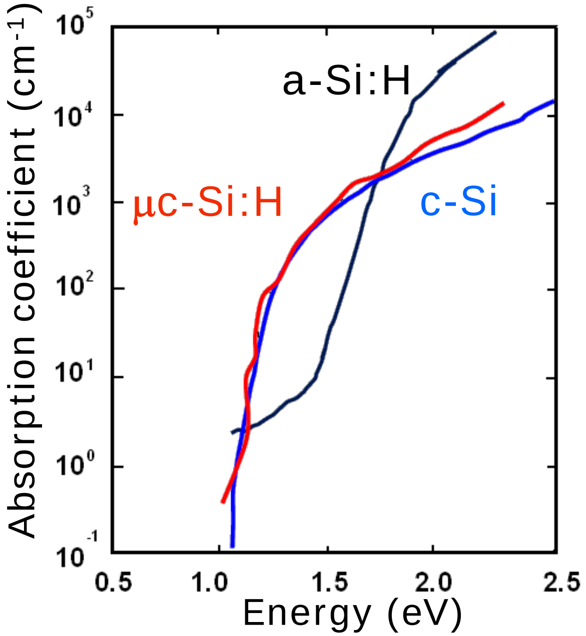


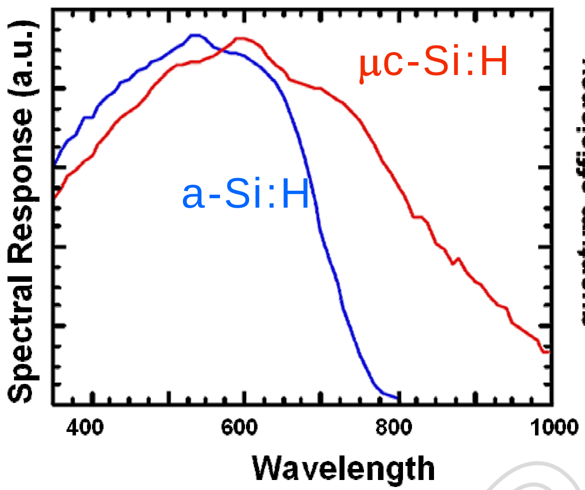
Dangling bond

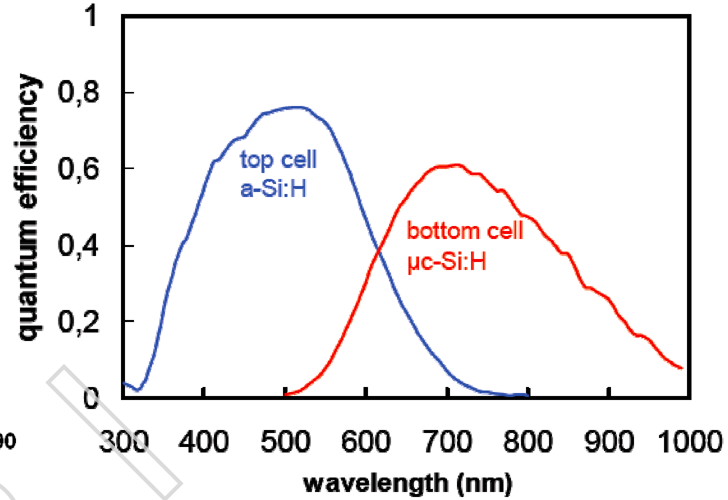
Si, Ge
Diamond structure

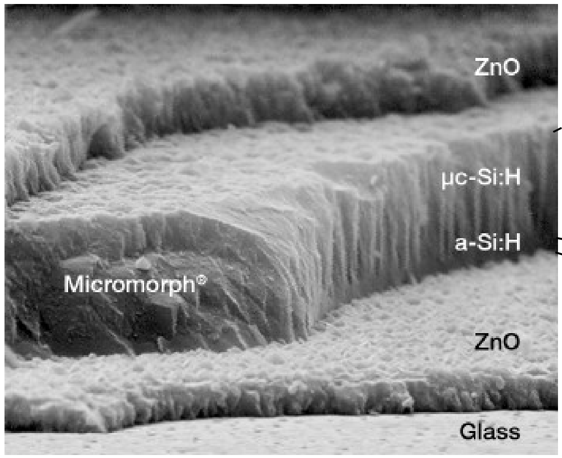


Micromorph a-Si:H / μc-Si:H tandem solar cell concept *(IMT Neuchâtel 1994)*

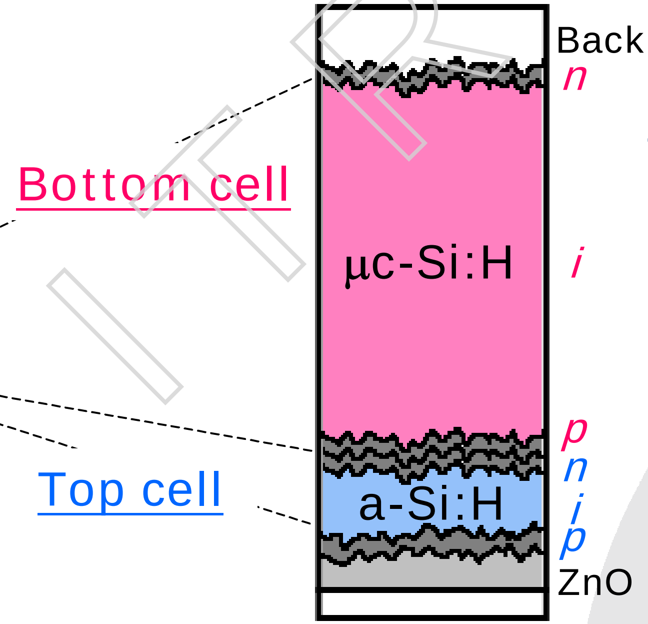








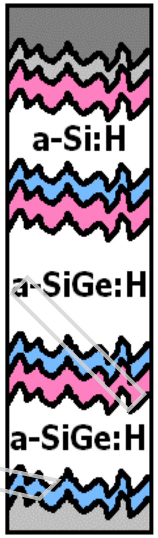
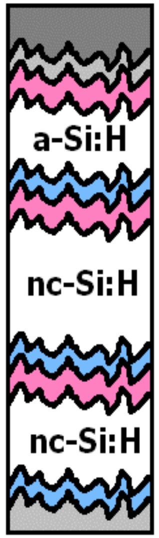
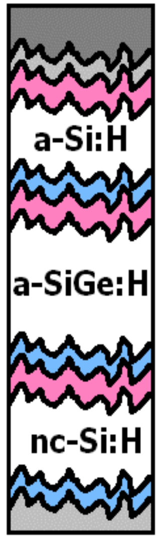
Courtesy of IMT SEM Micromorph



	Thickness	Bandgap
Bottom cell (μc-Si:H)	1.5-3 μm	1.1 eV
Top cell (a-Si:H)	0.2-0.3 μm	1.7 eV

Benchmarks

Small area cell (<1 cm^2)

single		tandem			triple		
							
a-Si	**μc-Si**	**a-Si/ μc-Si**	**a-Si/ poly-Si**	**a-Si/ a-SiGe**	**a-Si/ a-SiGe/ a-SiGe**	**a-Si/ nc-Si/ nc-Si**	**a-Si/ a-SiGe/ nc-Si**
IMT Oerlikon	**Kaneka**	**IMT Oerlikon**	**Kaneka**	**BP Solar, Sanyo**	**Uni-Solar**	**Uni-Solar**	**Uni-Solar**
10.1% (s) pin	**10.9% (i) pin**	**13.7% (i) pin 9.8 (i) nip**	**14.8% (i) 12% (s) pin**	**11.6% (i) 10.6% (s) pin**	**15.2% (i) 13.0% (s) nip**	**13.8% (i) 13.2% (s) nip**	**14.5% (i) 12.6% (s) nip**

Materials cost

gas *price* (per 1 liter)

SiH_4 : GeH_4 : H_2 = 1: 100: 0.05

Ref. A. Baumann, 2004

Process	Material	Utilization rate (%)	Cost ($/kg)	Thickness (μm)	Cost ($/W)
CdTe sublimation (commercial)	CdTe	75	170	4	0·05
CdTe electrodeposition (pilot line)	Te	95	250	2	0·02
In-line a-Si GD (commercial)	Ge	10	3000	1	0·12
Box carrier (batch) a-Si (commercial)	Ge	25	3000	1	0·05
High-rate a-Si (experimental)	Ge	10	3000	1	0·12
High-rate CIGS evaporation (experimental)	In	50	400	2	0·03
Sputtering CIGS (experimental)	In target	75	800	2	0·043
Silicon film[TM] (experimental)	Si	75	20	50	0·03
Single crystal silicon	Si (feedstock)	45	20	320	0·32

@ 1 μm

@ 50 μm

Ref. B.A. A'ndersson, Energy 23 (1998) 407-411.

Table 1. Materials requirements and indicators for the solar cells in four solar energy systems, each based on a specific thin-film technology supplying 100,000 TWh/yr.

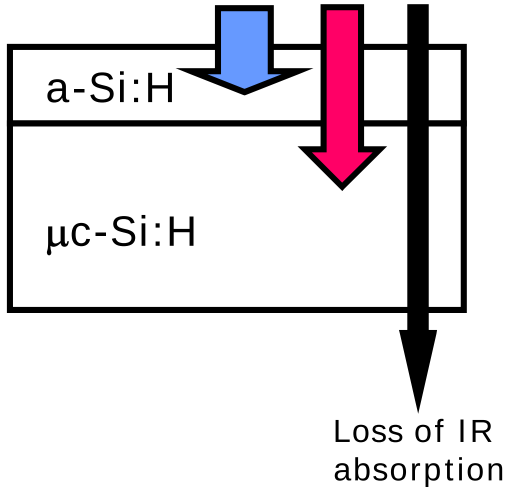
	Materials requirements (g/m²)	Total material requirements[b] (Gg)	Total material requirements /reserves[c]	Total material requirements /max. resources[d]	Annual material requirements[e] /refined materials[f]	Potential losses[g]/ weathered amounts[h]	Material cost share[i] (%)
a-SiGe[a]							
Sn	3.3	1700	0.20	0.004	0.079	2	0.04
Ge	0.22	110	51	0.0003	21	0.1	0.5
Si	0.54	270	Negligible	Negligible	0.0031	0.000002	0.002
Al	2.7	1400	0.00032	Negligible	0.00075	0.00005	0.008

A new concept of thin film μc-$Si_{1-x}Ge_x$:H solar cell

- **Advantages and opportunities**
- **Challenges**

Challenges of Si thin film solar cells

- Single junction　a-Si:H
- Tandem junction　a-Si:H/μc-Si:H
  - ➔ only absorbs VIS-near IR light
  - ➔ lower absorption coefficient in long wavelength
  - ➔ Light absorption is not enough in the infrared



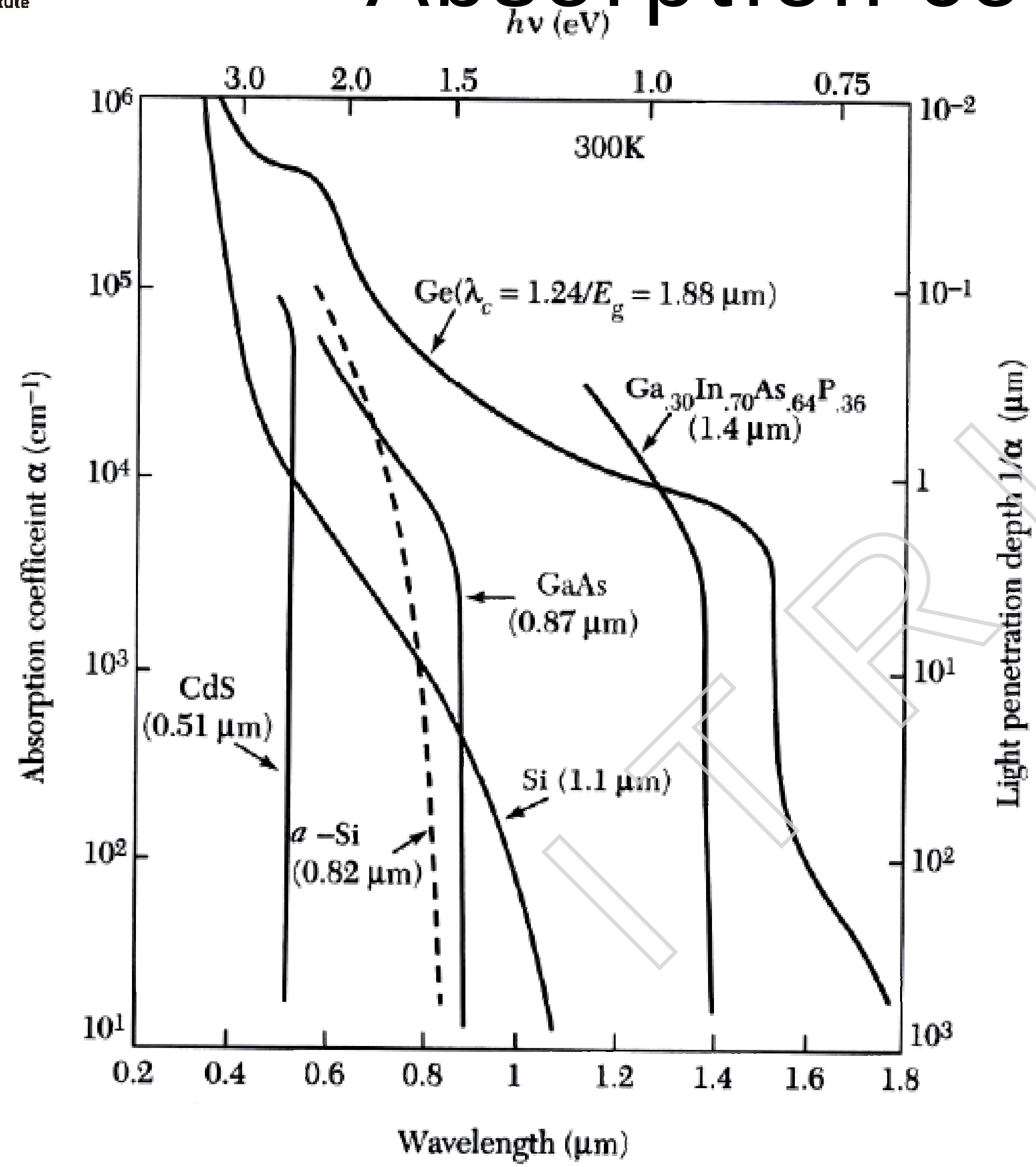
New concept of multi-junction solar cell

New candidate for a bottom cell material

$\mu c\text{-}Si_{1-x}Ge_x:H$

Ref. G. Ganguly, M. Kondo, A. Matsuda, APL, 69 (1996) 4224.

Absorption coefficient

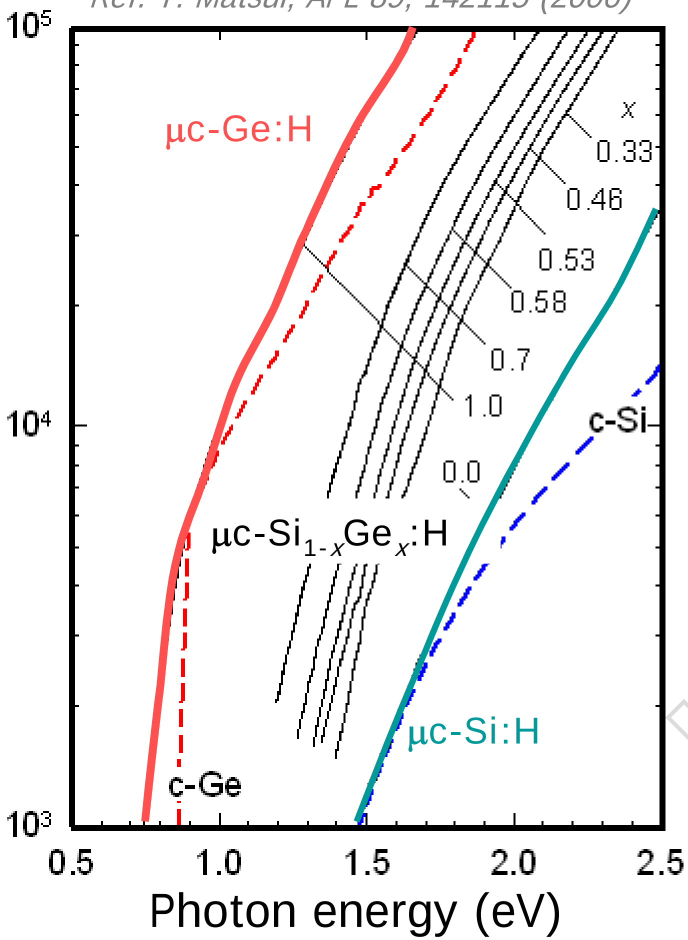


$A = 1 - \exp^{(-\alpha d)}$

$\alpha_{Ge} > \alpha_{Si}$

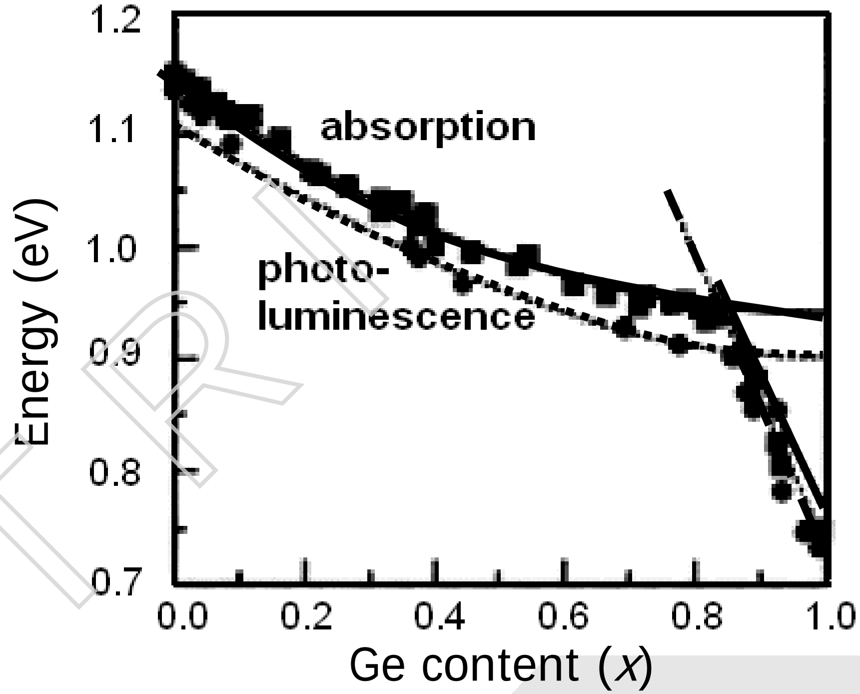
μc-$Si_{1-x}Ge_x$:H as narrow gap absorber for multi-junction solar cell

Ref. T. Matsui, APL 89, 142115 (2006)



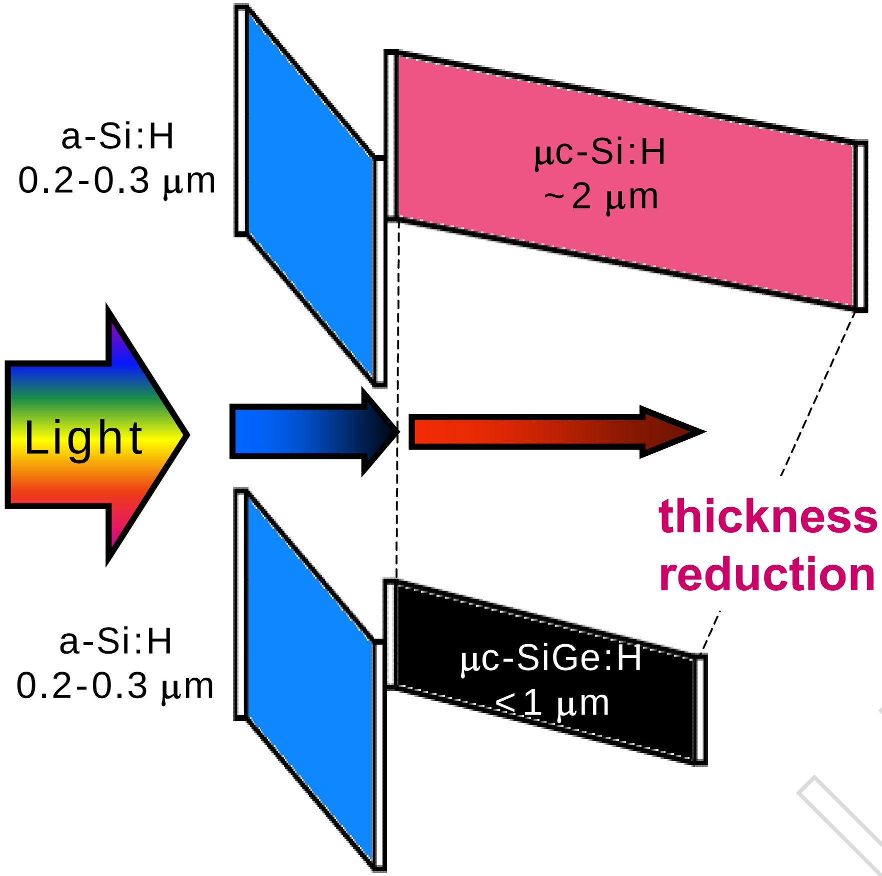
absorption coefficients
μc-$Si_{1-x}Ge_x$:H > μc-Si:H

Ref. Braunstein et al. (1958) and Weber & Alonso (1989)



Tunable bandgap of
μc-$Si_{1-x}Ge_x$:H
E_g ~ 1.1 - 0.7eV

Why Silicon-Germanium Thin Film?



tandem junction

μ_{ini} = 11.2% @ d_{bottom} = 0.9 μm

Ref. T. Matsui and M. Kondo, AIST (2009)

Thickness μc-Si:H >> a-Si:H

μc-Si:H is 10 times thicker than a-Si:H

Deposition rate μc-Si:H << a-Si:H

High-rate deposition technique

VHF and HPD (high-pressure depletion) plasma CVD

Bottom cell should be made as thin as possible

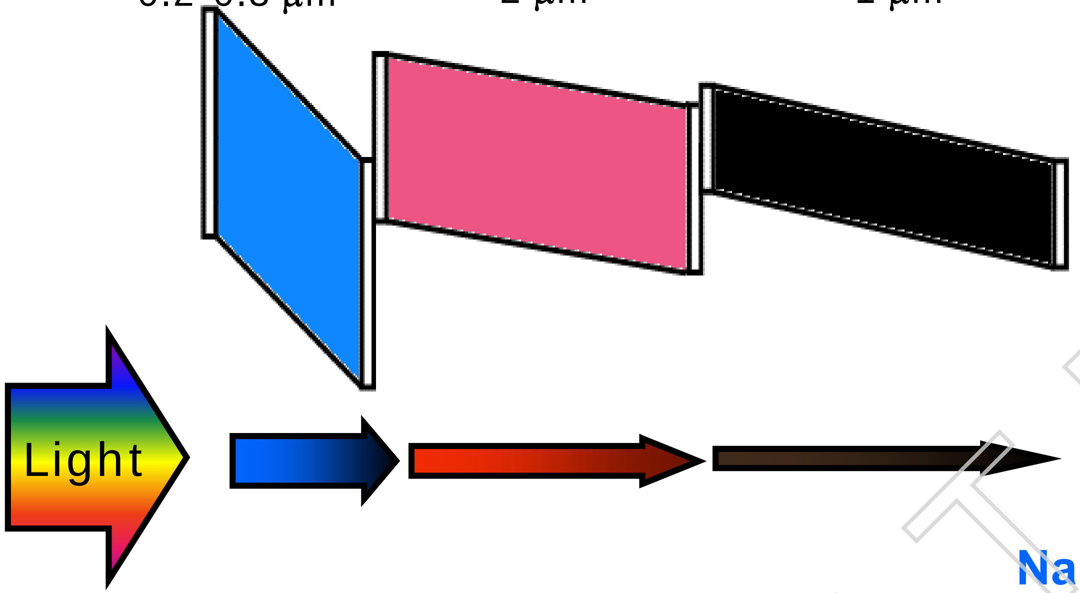
μc-Si:H

↓

μc-$Si_{1-x}Ge_x$:H

- Short deposition time
  - ⇨ Industrially advantageous
- Less film thickness
  - ⇨ Acceptable to flexible solar cells
- Increased long wavelength and IR absorption
  - ⇨ Enhanced solar cell efficiency

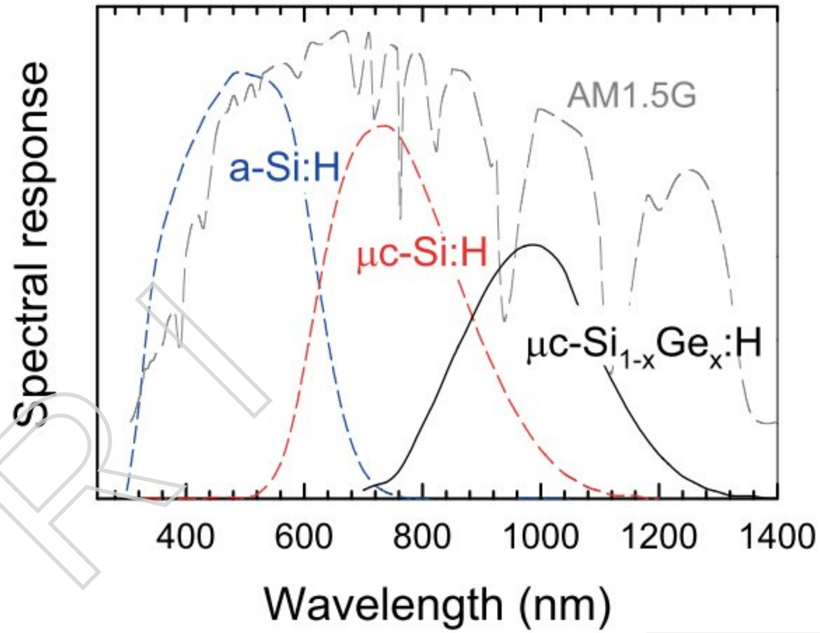
Advantages of μc-SiGe thin film solar cell



Triple junction

μ_{ini} = 11.6 %

Ref. T. Matsui and M. Kondo (2010/08 AIST成果發表會)



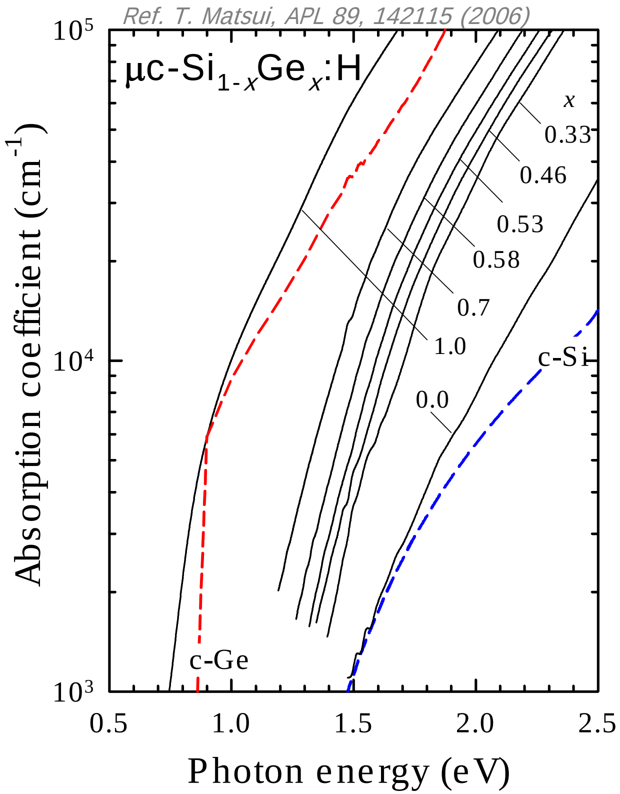
Narrow bandgap material μc-SiGe:H bottom cell application in triple junction

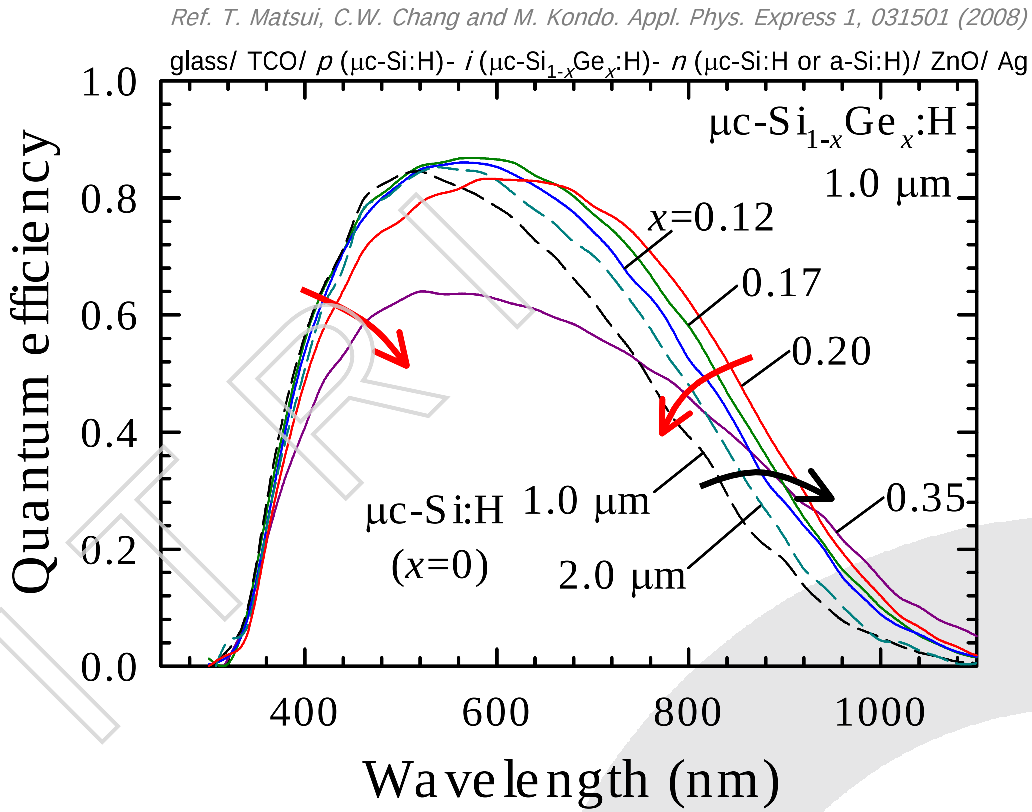
a-Si:H/μc-Si:H/μc-$Si_{1-x}Ge_x$:H

Increased NIR absorption
Enhanced solar cell efficiency

Issues of μc-$Si_{1-x}Ge_x$:H

- x = 0-0.2 ⇨ IR sensitivities increase monotonically
- x > 0.1-0.2 ⇨ IR sensitivities of μc-$Si_{1-x}Ge_x$:H (1μm) > μc-Si:H (2μm)



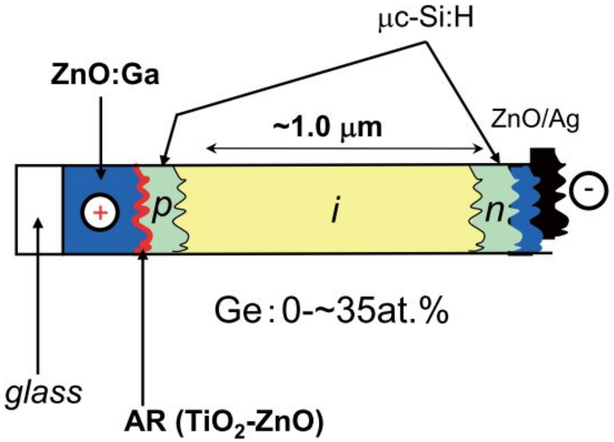


x > 0.2 ➔ solar cell performance degrades drastically

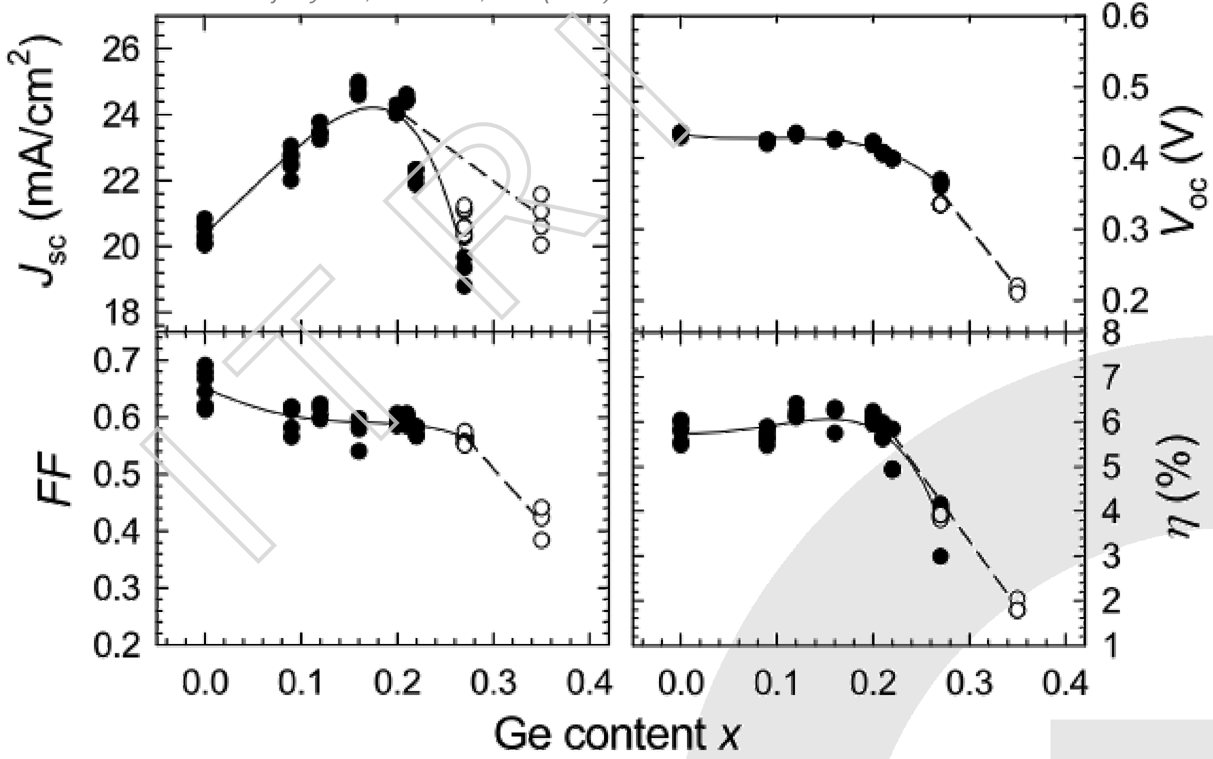
Problems of μc-$Si_{1-x}Ge_x$:H

- x = 0.15-0.2 ⇨ *Jsc max.*
  ⇨ *Jsc gain ~5 mA/cm²*
- x>0.2 ⇨ solar cell performances decrease
  (charged Ge dangling bonds increase ?)

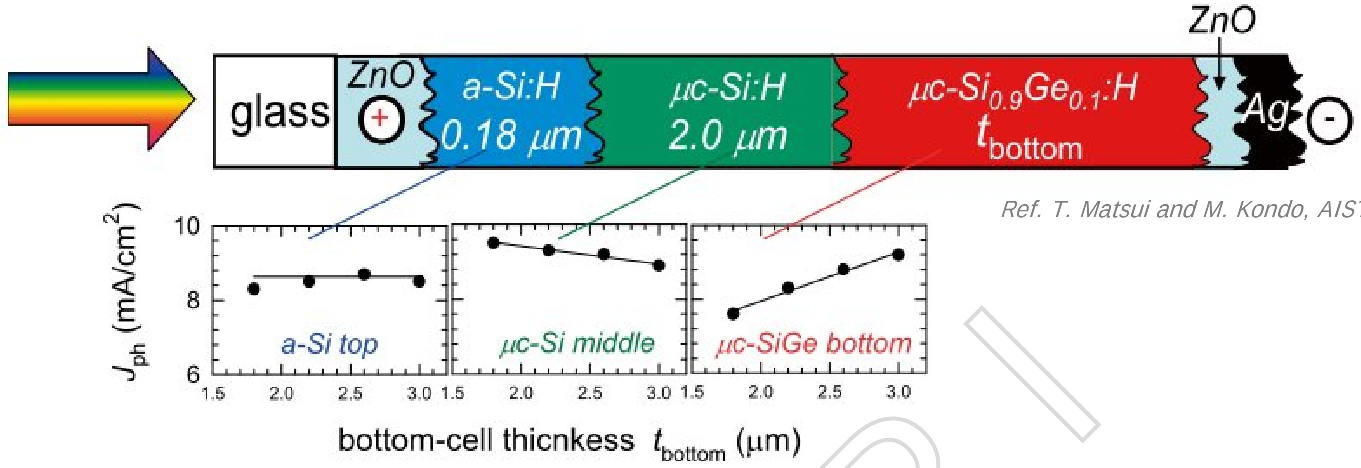
Ref. T. Fujibayashi, M. Kondo, APL (2006)



Ref. T. Fujibayashi, M. Kondo, APL (2007)



Performance of triple junction of a-Si:H/μc-Si:H/μc-$Si_{1-x}Ge_x$:H



Ref. T. Matsui and M. Kondo, AIST (2010)

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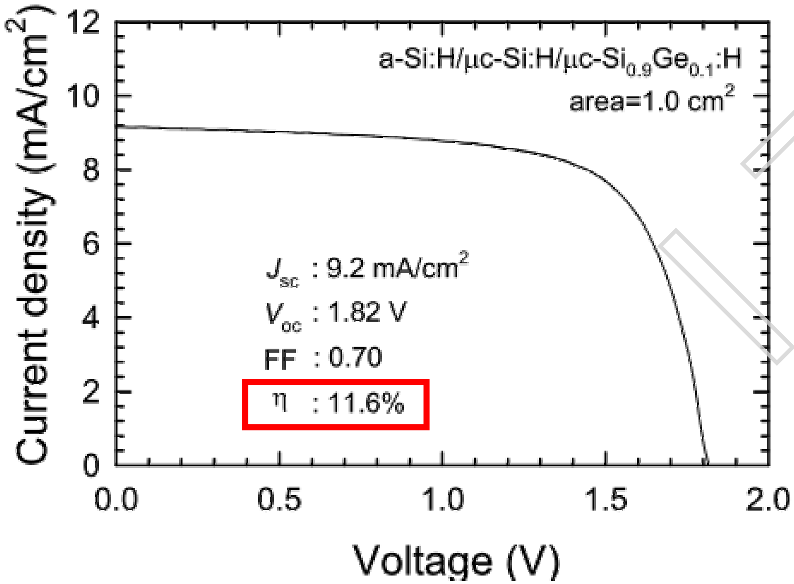
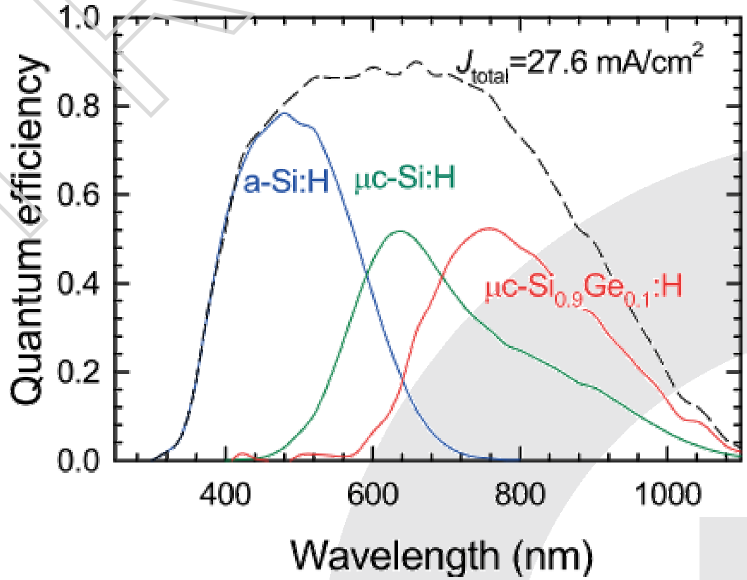


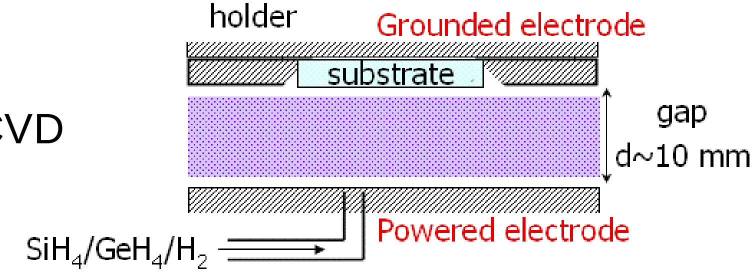


Properties of μc-$Si_{1-x}Ge_x$:H thin films

- **ESR spin densities (neutral dangling bonds)**
- **Carrier densities**

Methods and Experiments

VHF PECVD



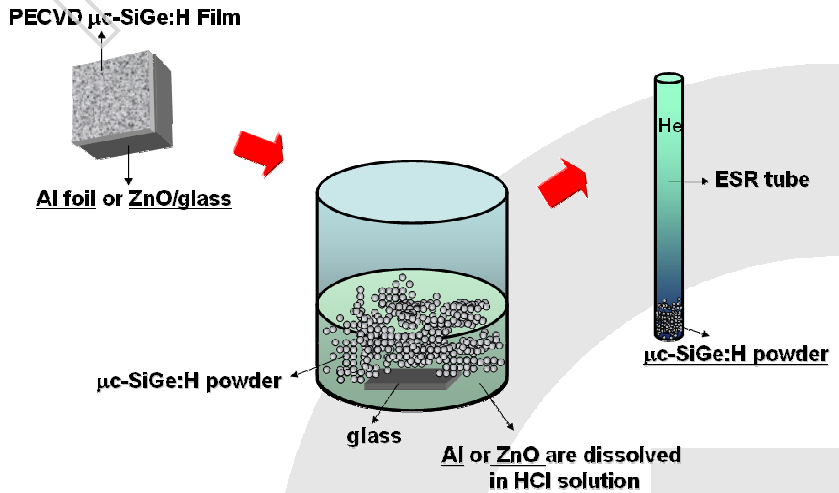
– Raman measurement –

- He-Ne laser (λ =633 nm)

– ESR measurement –

- Powdered samples (10-40 mg) were obtained by HCl etching of μc-SiGe:H films grown on ZnO/glass substrates.
- ESR measurements were performed at room temperature in an X-band (~9.5 GHz) spectrometer.
- Defect density was determined by measuring the spin numbers of the $CuSO_4 \cdot 5H_2O$ used as a standard sample.

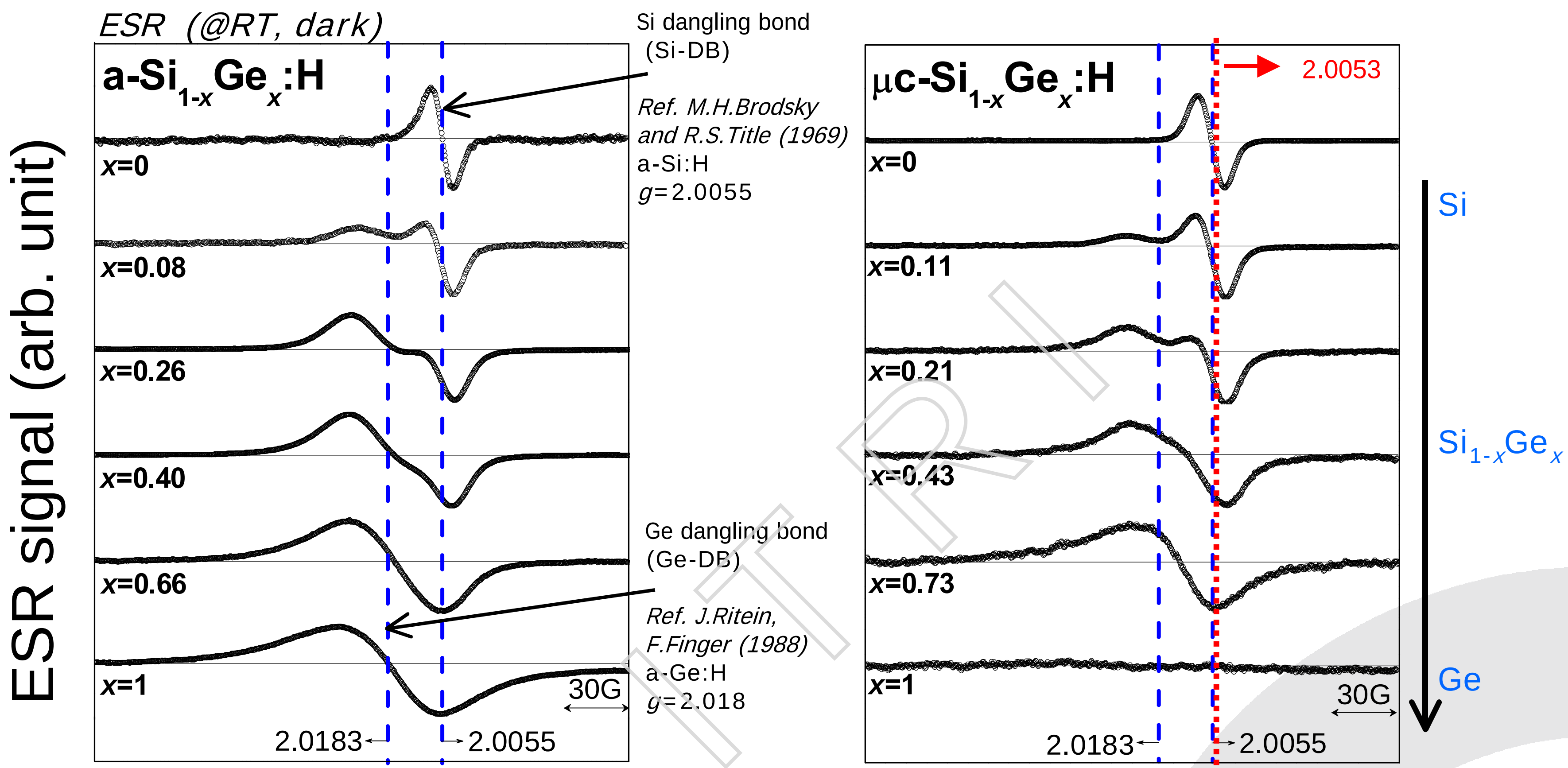
ESR
Electron Spin Resonance



– Hall-effect measurement –

- Hall-effect measurements were performed at room temperature using Van der Pauw method.

ESR spectra of a-SiGe:H and μc-SiGe:H thin films for various Ge contents



a-Si:H ➔ g=2.0055 ; ΔHpp=7.7G
a-Ge:H ➔ g=2.0183 ; ΔHpp=43.9G

μc-Si:H ➔ g=2.0053 ; ΔHpp=7.5G
μc-Ge:H ➔ undetected

C.W. Chang, Ph.D thesis, Tokyo Institute of Technology, 2009.
C.W. Chang, T. Matsui, M. Kondo, J. Non-cryst. solids, 354 (2008) 2365.*

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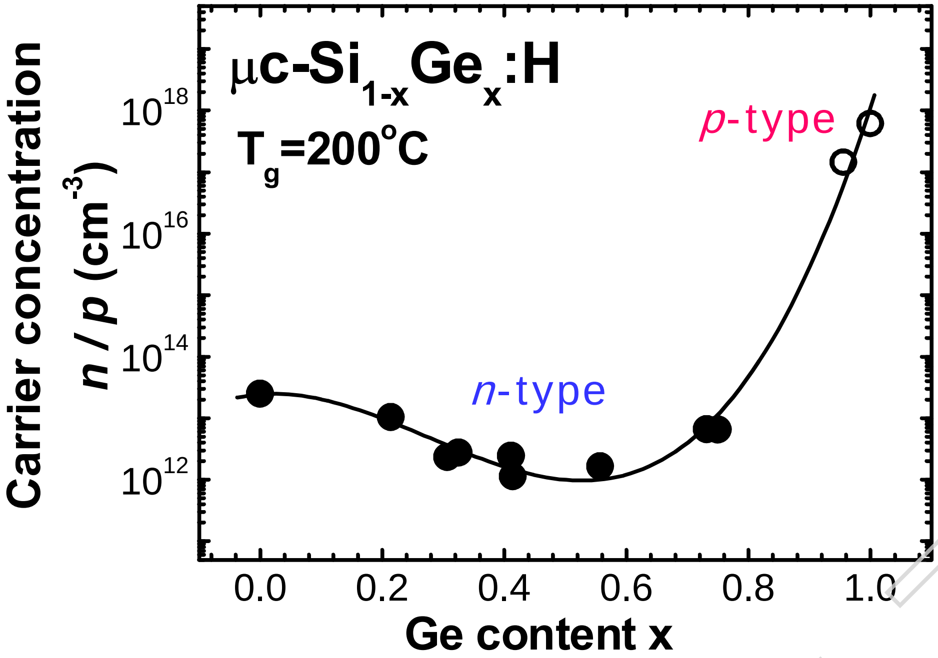
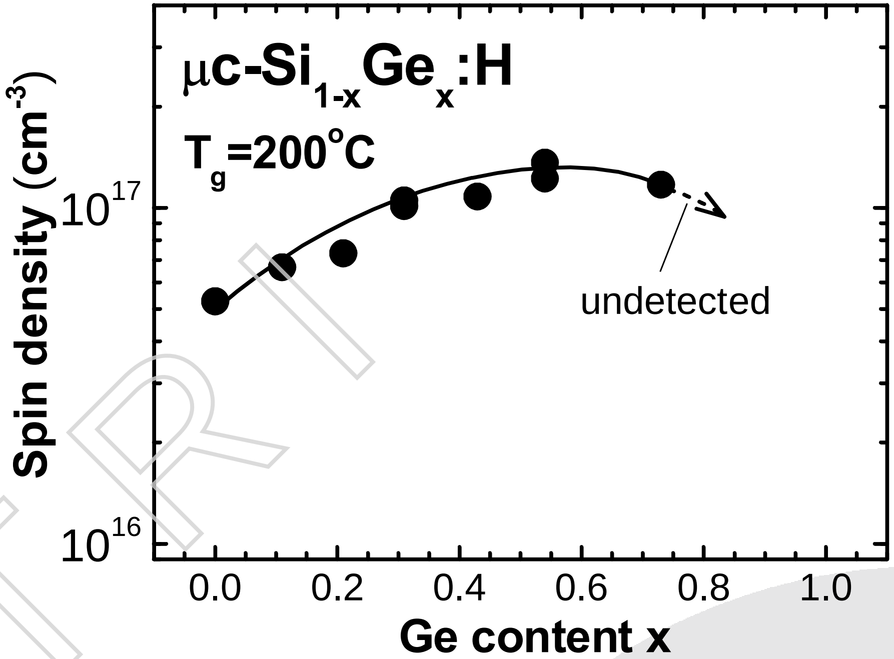
Carrier concentration and neutral defect density of μc-SiGe

Carrier concentration vs. Ge content

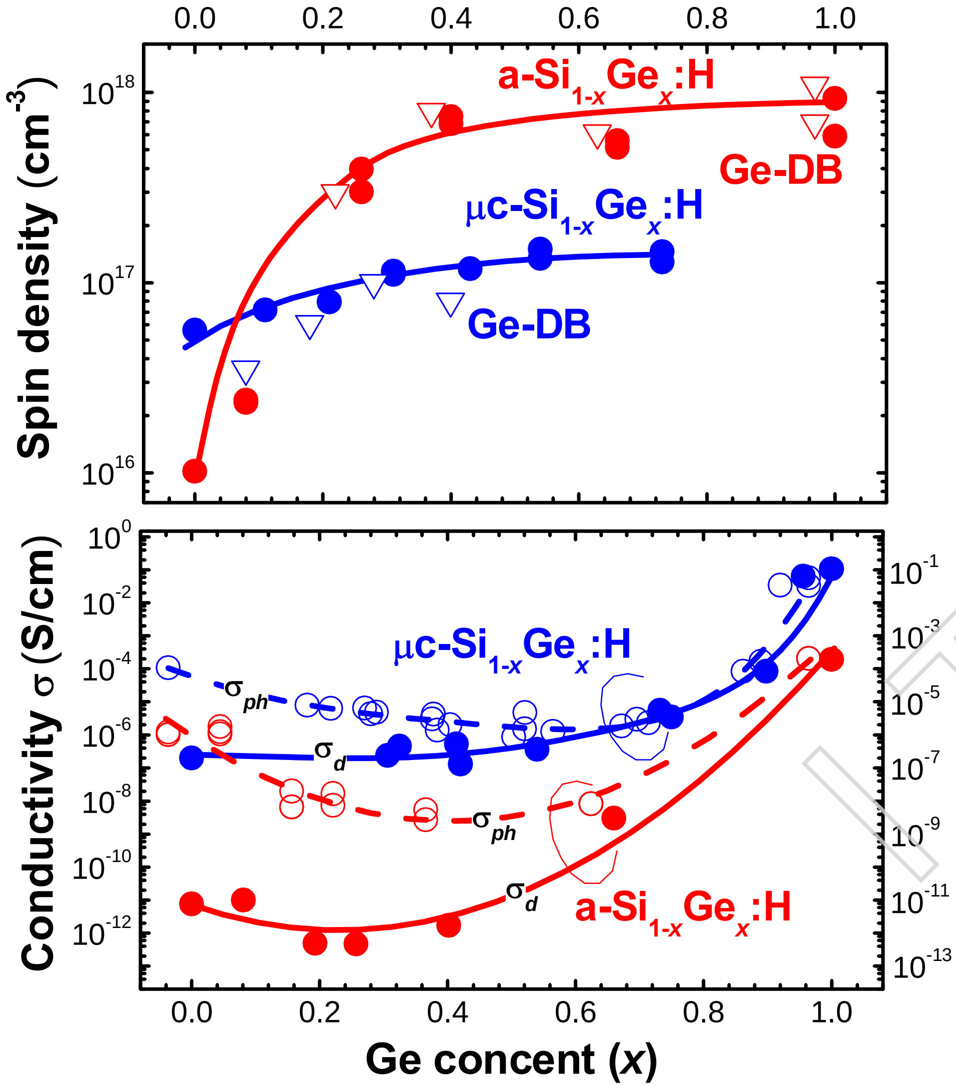


Spin density vs. Ge content



- Ge-rich ➔ strong *p*-type: Ge incorporation induces an acceptor state generation (probably at grain boundary)
  - ⇨ Fermi level shift toward the valence band edge.
- ESR signal was undetected when the carrier concentration became comparable to dangling bond density.

Electrical properties of a-SiGe and μc-SiGe:H with various Ge contents



C.W. Chang, T. Matsui, M. Kondo, J. Non-cryst. solids, 354 (2008) 2365.

- Spin density↑⇨ photoconductivity↓
- The smaller Ge-DB density of $\mu c\text{-}Si_{1-x}Ge_x:H$ is consistent with high photoconductivities

Ge-DB acts as a predominant recombination center

Conclusions

1. Ge incorporation provides an enhanced infrared light absorption.
2. Solar cell performances decreases with increasing Ge contents.
3. Ge dangling bonds are charged in large densities due to the presence of the acceptor states in undoped μc-$Si_{1-x}Ge_x$:H.
4. The neutral Ge dangling bond acts as a predominant recombination center.
5. Defect states (dangling bonds) in **μc-$Si_{1-x}Ge_x$:H** as an acceptor state closed to valence band, which are located at grain boundaries.

Ge dangling bond passivation?
Acceptor states compensate?

Thanks for your attention.

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Nov. 15, 2010