

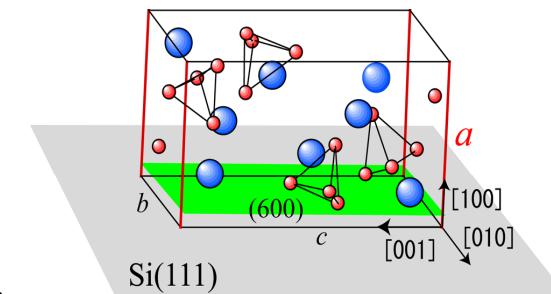
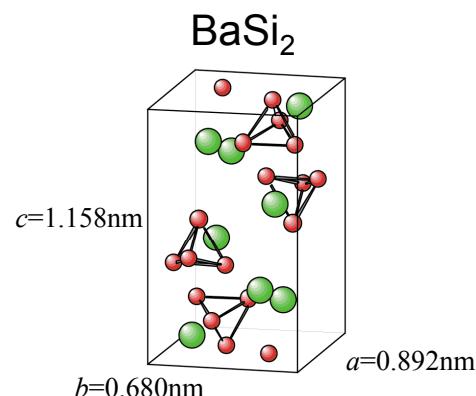
シリコンベース新材料を用いた 薄膜結晶太陽電池を目指して



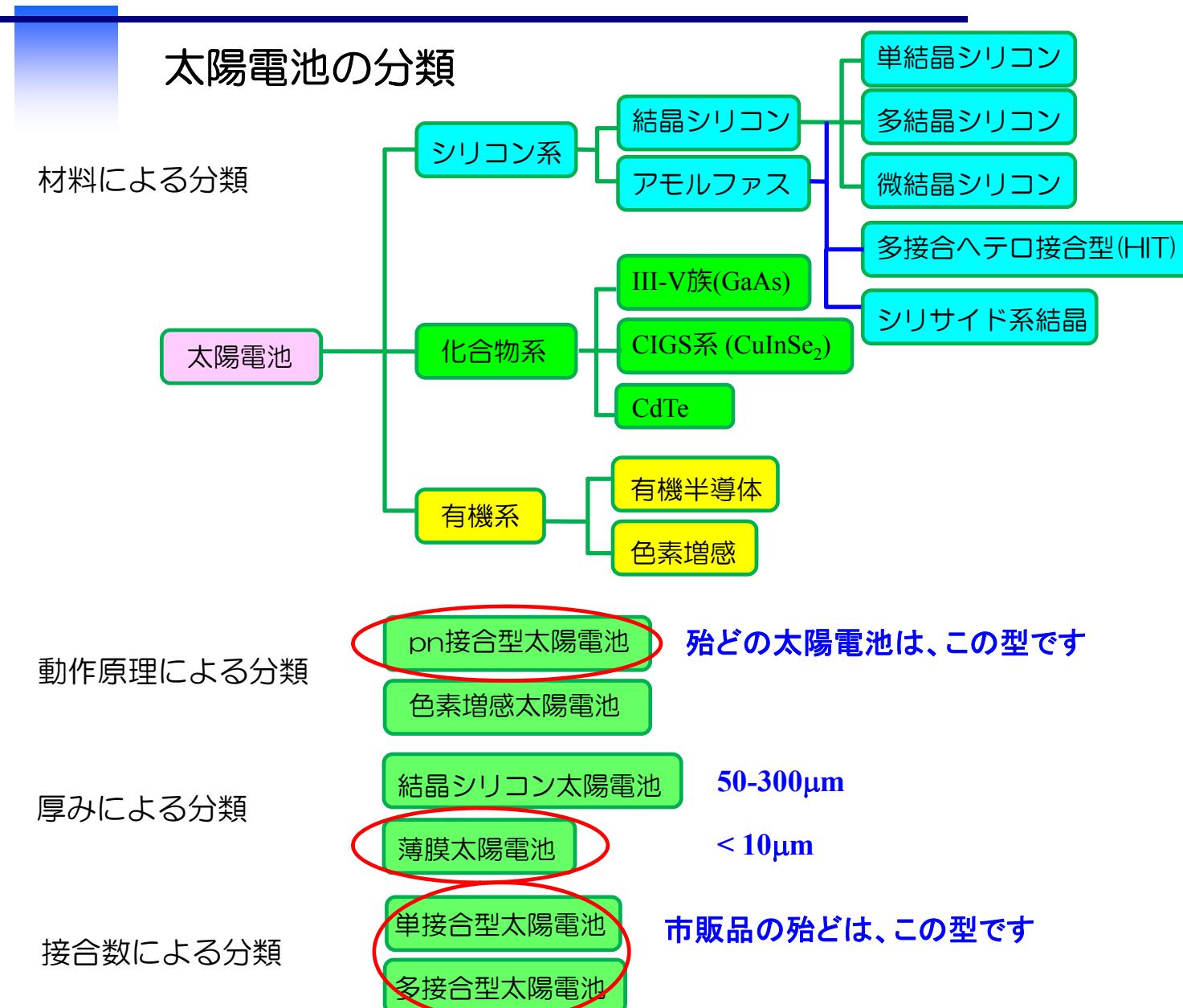
筑波大 数理物質科学研究科 電子・物理工学専攻
JST-PRESTO



末益 崇

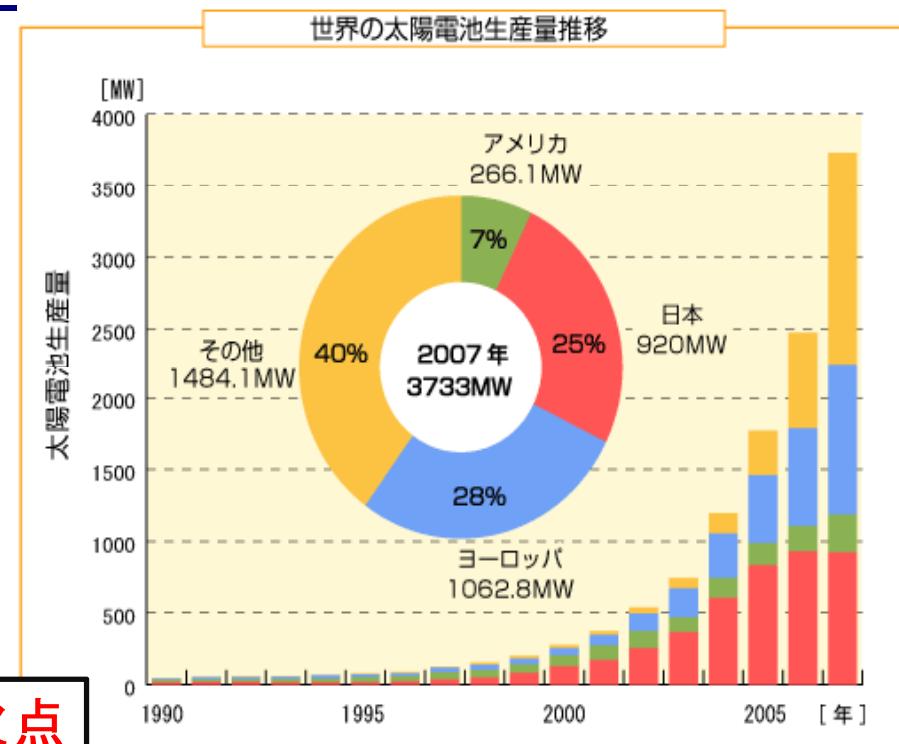
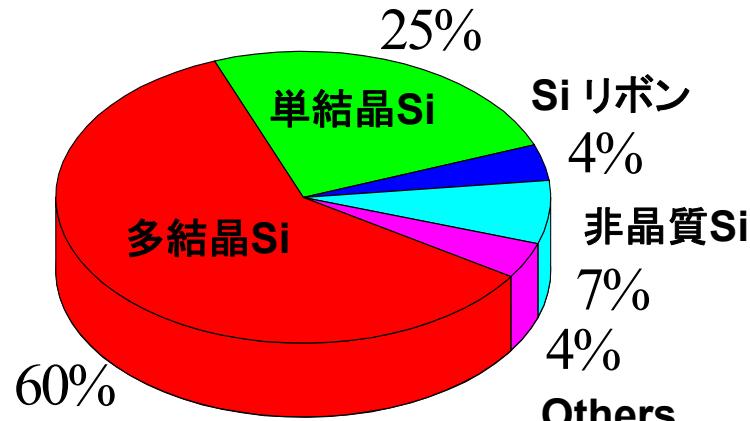


Jan. 25, 2010 日本板硝子工学助成会



太陽電池の現状

太陽電池用の半導体材料(Siが95%)



Siの利点

- ・資源が豊富
- ・成熟した技術

Siの欠点

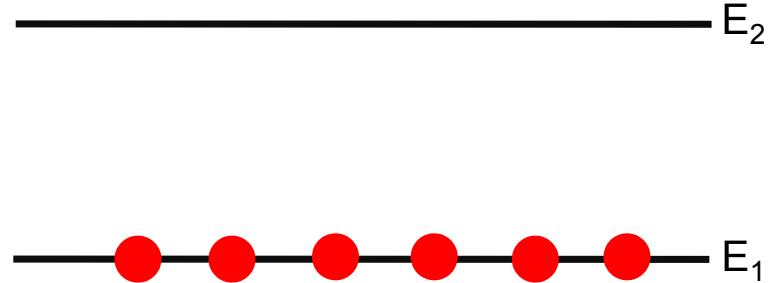
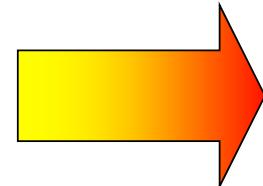
- ・光吸収係数が小さい⇒厚い太陽電池
Siの大量消費(50μmは必要)
安定確保が困難
- ・禁制帯幅Egが小さい
(理想値Eg=1.4eV vs Egsi=1.1eV)

将来進むべき方向

資源の豊富な元素で構成される、高効率 & 薄膜太陽電池

光のエネルギーを吸収するとは？

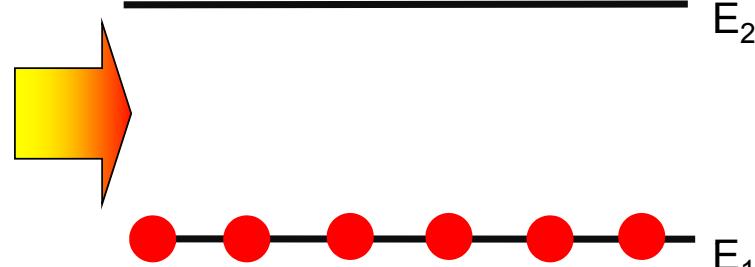
$$(光のエネルギー) = (E_2 - E_1)$$



エネルギー

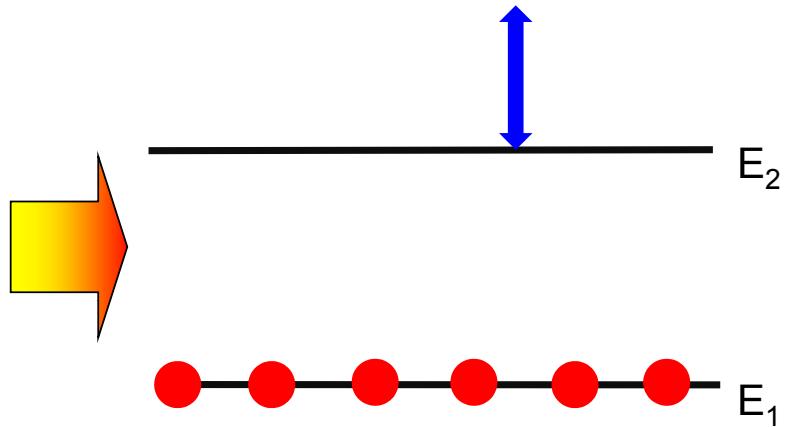
$$(光のエネルギー) < (E_2 - E_1)$$

光は吸収されない

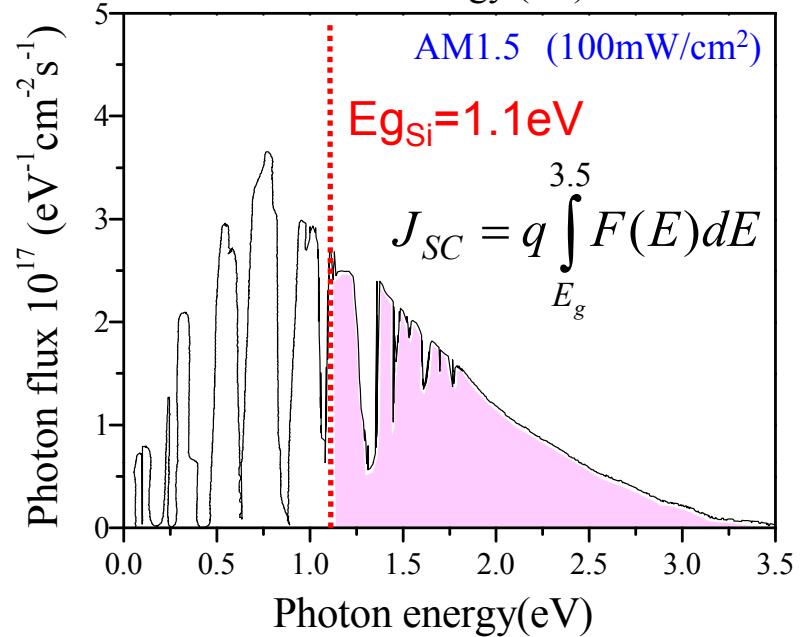
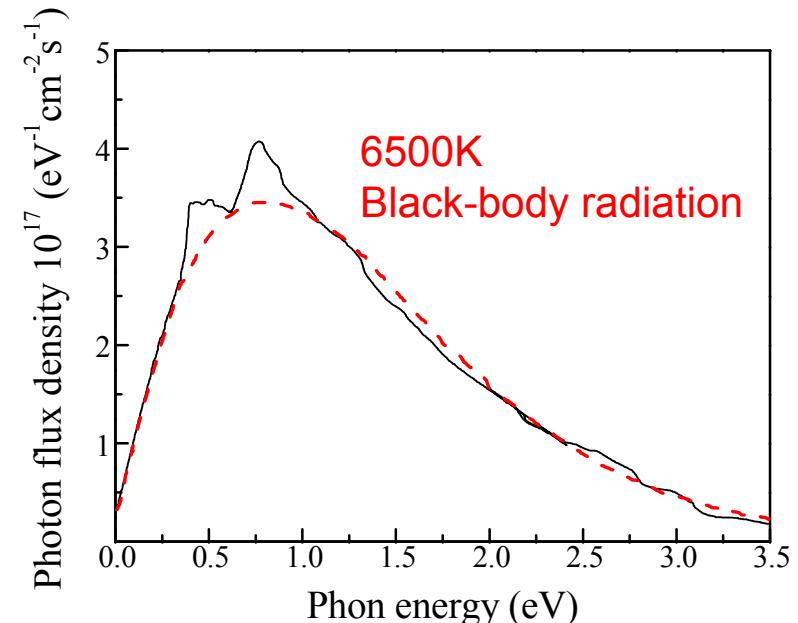
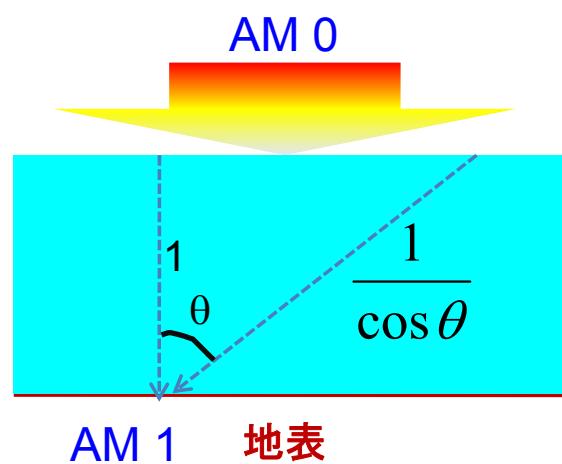


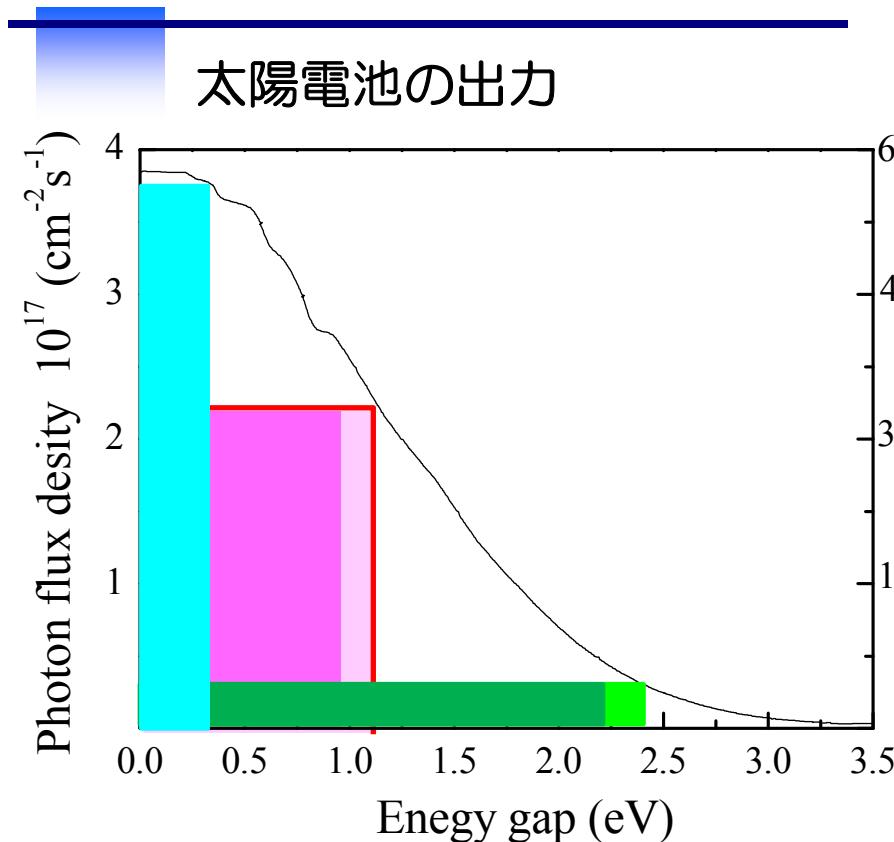
$$(光のエネルギー) > (E_2 - E_1)$$

余分なエネルギーが無駄になる

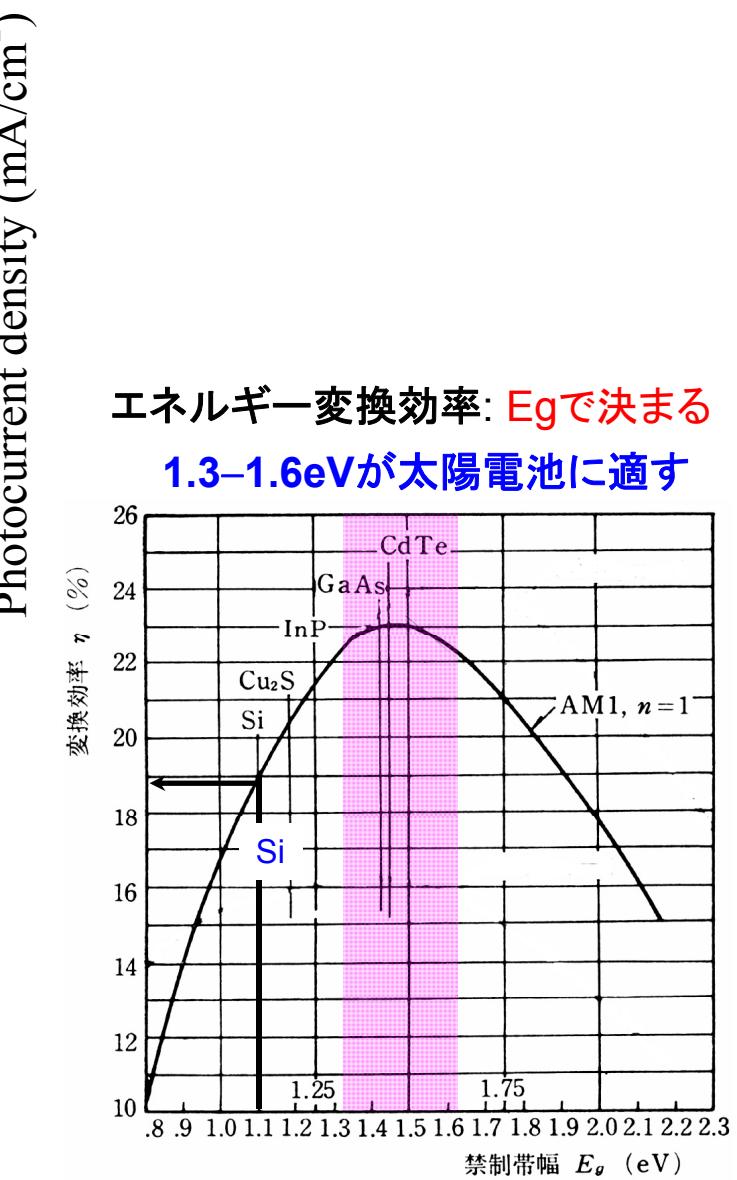


太陽光のスペクトル





$$\eta \approx \frac{J_{\text{photo}}(\text{mA}/\text{cm}^2) \times qE_g \times 0.8}{100(\text{mW}/\text{cm}^2)} = 28\%$$



BaSi₂の特徴

目標: Si系薄膜結晶太陽電池 on SiO₂
Si-based crystalline thin-film solar cells on SiO₂

✓ 禁制帯幅が太陽電池に相応しい

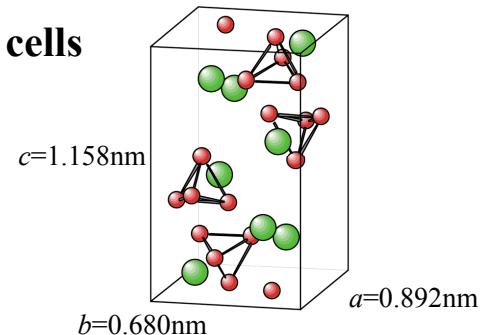
Eg: 1.3 eV (BaSi₂)~1.4 eV (Ba_{0.5}Sr_{0.5}Si₂) suitable for solar cells

⇒High efficiency solar cell

Nakamura, ..., Suemasu, *APL* **81** (2002) 1032.

Morita, ..., Suemasu, *JJAP* **45** (2006) L390.

(Theory) Imai and Watanabe, *TSF* **515** (2007) 8219.



✓ 光吸収係数が大きい

Very large optical absorption coefficient α

$\alpha \sim 10^5 \text{ cm}^{-1}$ at 1.5 eV

More than 100 times larger than crystalline Si

⇒Thin-film solar cell

Morita, ..., Suemasu, *TSF* **508** (2006) 363.

(Theory) D. B. Migas *et al*, *PSS (b)* **244** (2007) 2611.

✓ 資源が豊富

Si & Ba abundant chemical elements

Clarke number: Si(2), Ba(14), Sr(15)

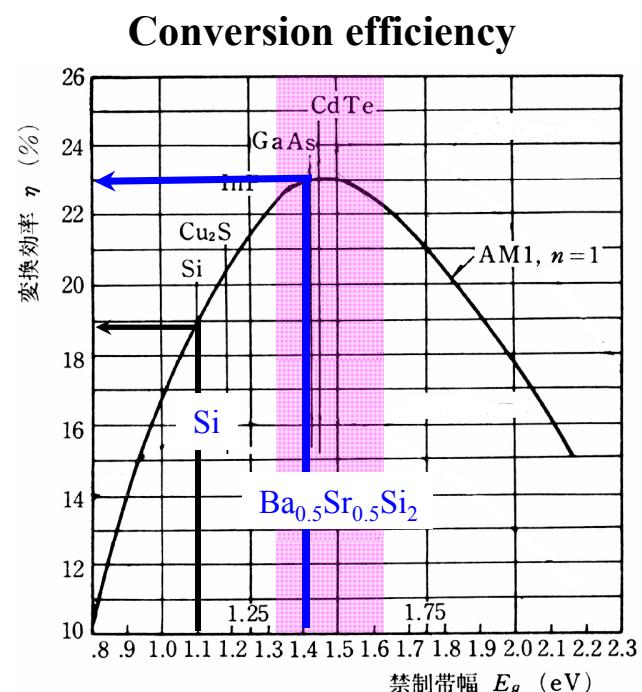
cf. CIGS: Cu(26), In(66), Ga(35), S(16), Se(69)

✓ Si(111)面にエピタキシャル成長可能

Epitaxial growth possible on a Si(111) surface

⇒High-quality crystal growth

Inomata, ..., Suemasu, *JJAP* **43** (2004) 4155, L478, L771.

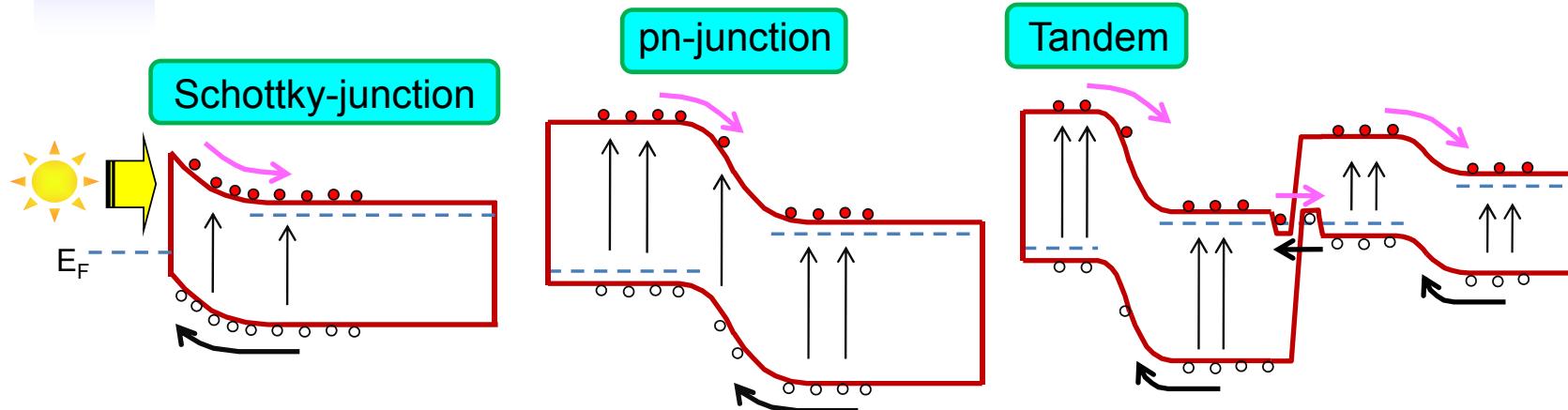


他の太陽電池材料との比較：特徴は何か？

Characteristic points of BaSi₂ compared with other materials

項目	BaSi ₂ 系	結晶 Si 系	薄膜 Si 系	CIS 系	CdTe	III-V 族 集光多接合	有機
太陽光との整合： バンドギャップ	○ 1.4eV に制御可	△ 1.1eV	○ 1.7eV(a-Si) 1.1eV(μ-Si)	○ 1.4eV に制御可	○ 1.4eV	○ 0.66~2.0eV	○ 1.0~2.0eV
資源量 (地殻中存在順位)	○ Si:2位 Ba:14位 Sr:15位	○ Si:2位	○ Si:2位	✗ In:65位 Se:66位	✗ Cd:62位 Te:70以下	✗ Ga:34位 As:51位	△ Ti:9位 I:58位
光吸收層の膜厚	○ 1μm程度	✗ 100 μm以上	△ 数~10 μm	○ 数μm	○ 数μm	○ 数μm	○
長期安定性 光劣化	○ 光劣化なし	○	△ 光劣化	○	△ 電極材拡散	○	✗
結晶品質	○ 高品質エピタキシャル	○ 高品質バルク結晶	△ アモルファス+微結晶	△ 微結晶	△ 微結晶	○ 高品質エピタキシャル	△ アモルファス+微結晶
コメント	・低環境負荷 ・基盤技術の確立が必要	・成熟技術 ・実用太陽電池の 90%	・高スループット	・高変換効率	・高変換効率 ・Cd の安全性に懸念	・超高効率 ・集光、追尾機構が必要	・高効率化、耐久性向上が課題

研究項目



1. 不純物ドーピングによる伝導型、キャリア密度制御
Control of electron and hole concentrations by impurity doping

2. 分光感度特性

Photoresponsivity

3. BaSi₂/Siトンネル接合の形成

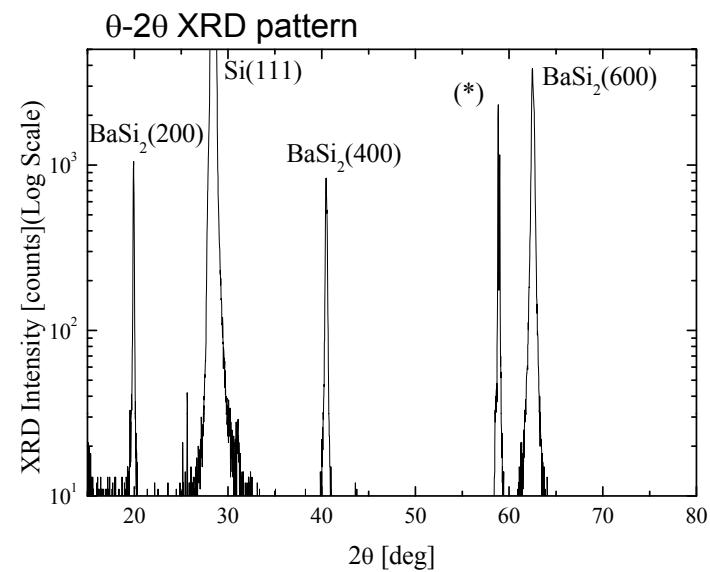
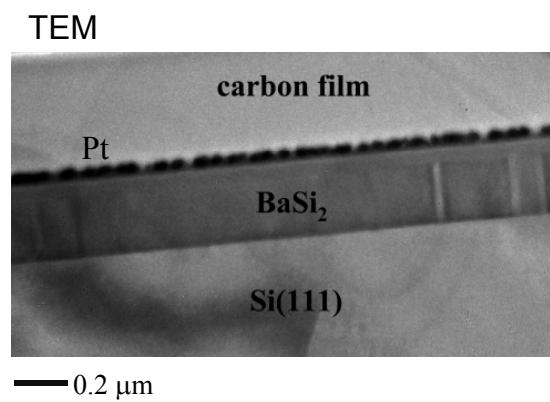
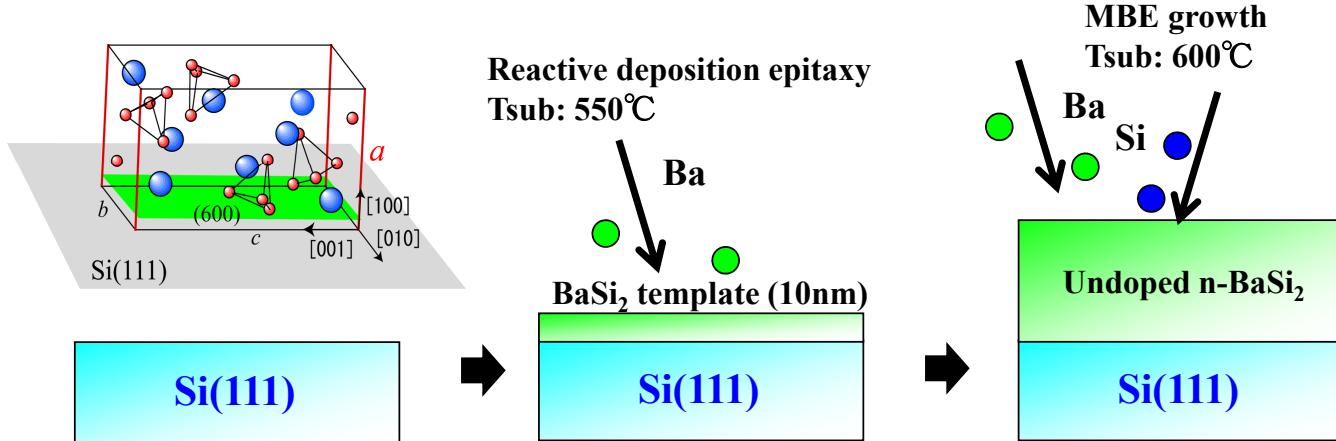
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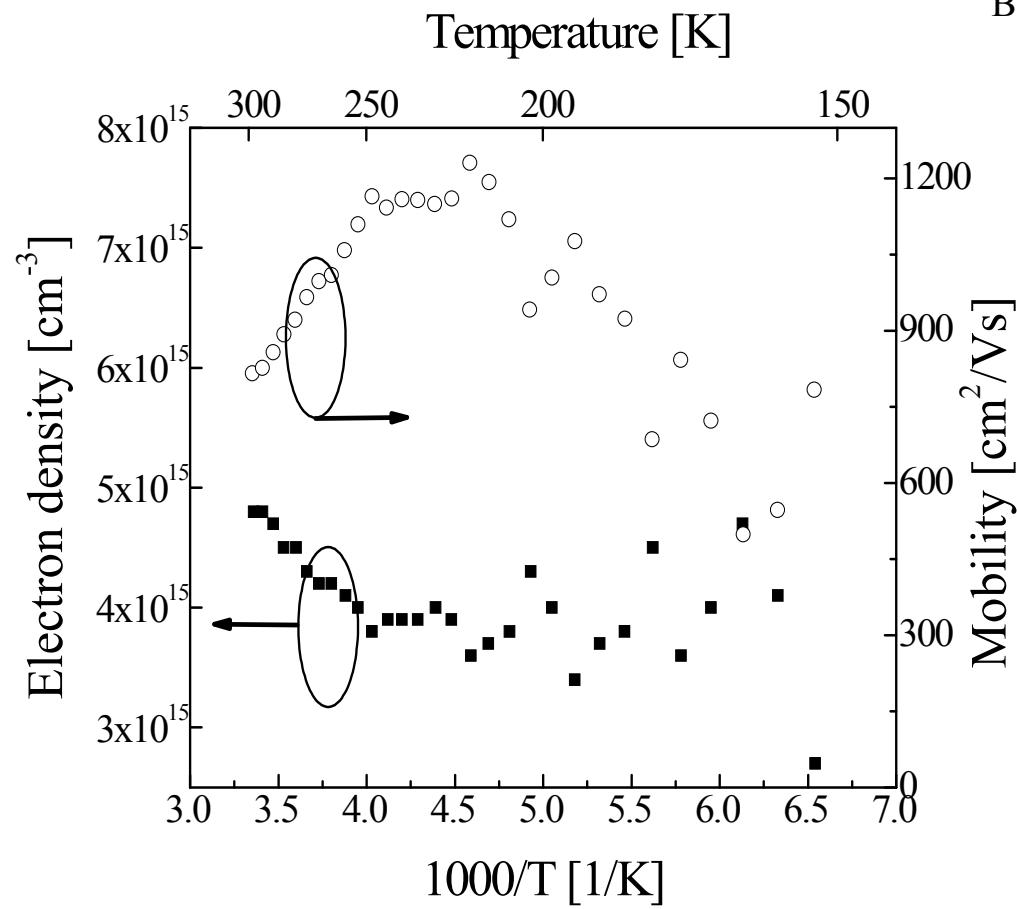
Demonstration of solar cell

Growth of BaSi₂ epitaxial films using a template layer

Inomata,..,Suemasu, *Jpn. J. Appl. Phys.* **43** (2004) 4155, L478, L771.

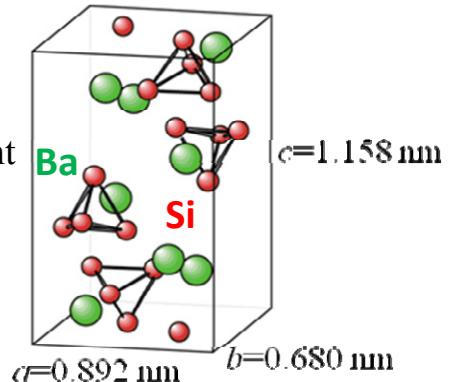


Electrical properties of undoped BaSi₂ film



Zintl phase (A_aX_x)

Si-Si: covalent
Ba-Si: ionic



Baサイトより、Siサイトが置換されやすい
Y. Imai *et al.*, *Intermetallics* **15** (2007) 1291

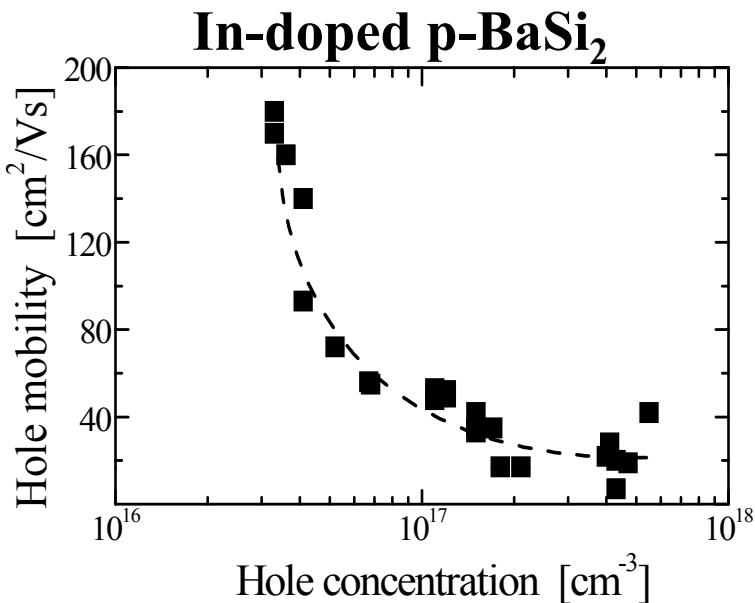
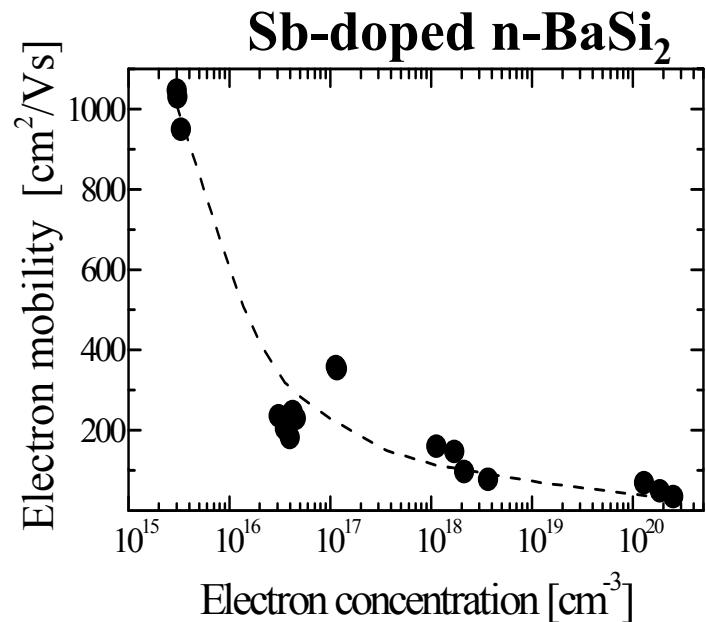
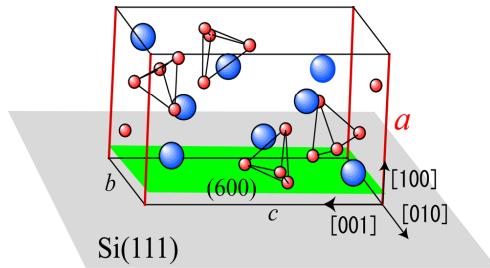
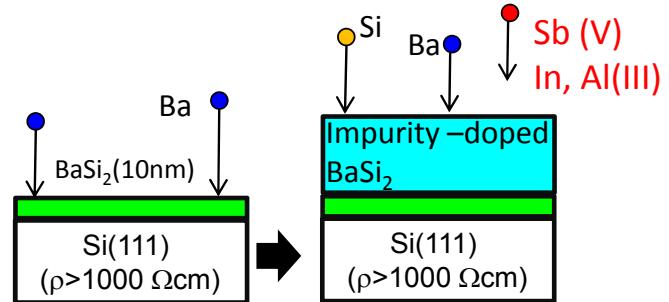
Periodic table highlighting elements in the Zintl phase A_aX_x . Elements are grouped into columns 13, 14, and 15. A blue box surrounds Al, while red boxes surround Si, P, As, and Sb. Other elements in the same columns are in green boxes: Rb, Cs, Fr; Ba, La; Y, In; N, P; and Sb.

1	2	3
Rb	Ba	La
Cs		
Fr	In	
	Y	
		N
	Al	Si
		P
		As
		Sb

Morita, ..., Suemasu, *Thin Solid Films* **508** (2006) 363.

Electrical properties of impurity-doped BaSi₂ films

Kobayashi,.... Suemasu, *Thin Solid Films* **515** (2007) 8242.
 Kobayashi,.... Suemasu, *Appl. Phys. Express* **1** (2008) 051403.



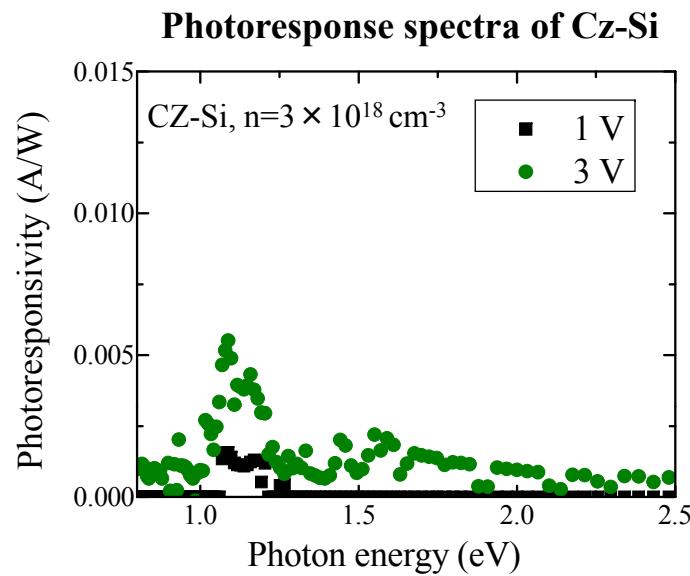
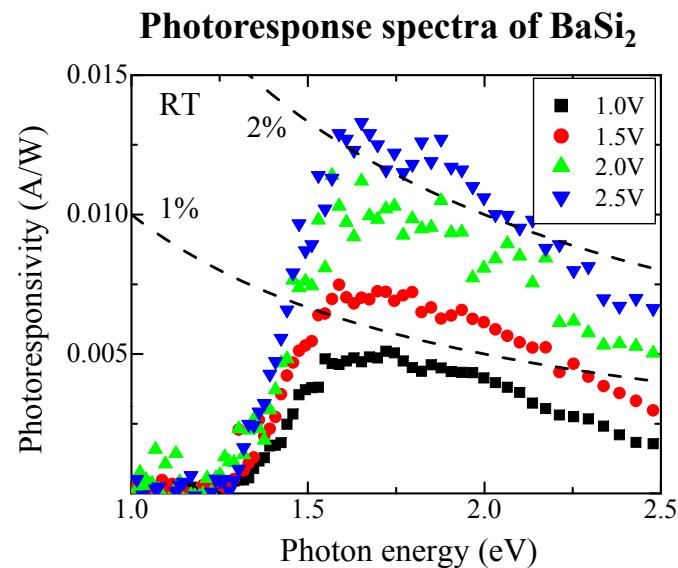
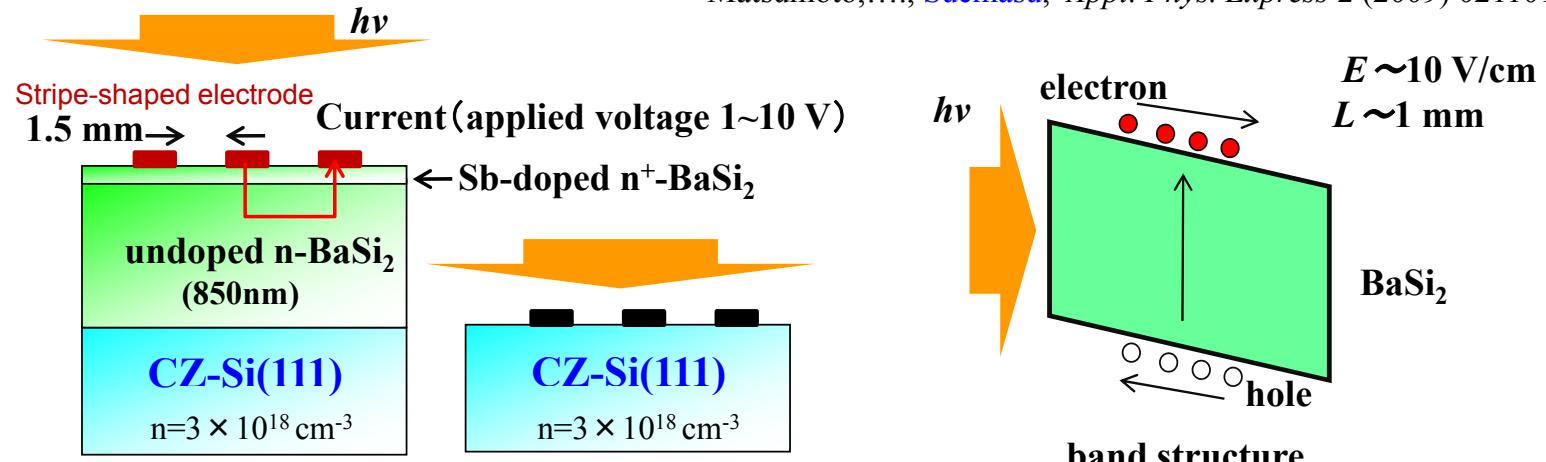
1. 不純物ドーピングによる伝導型、キャリア密度制御
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2. 分光感度特性
Photoresponsivity

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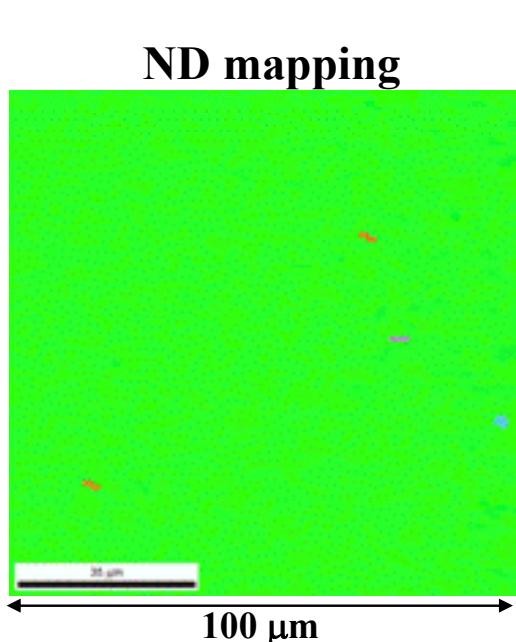
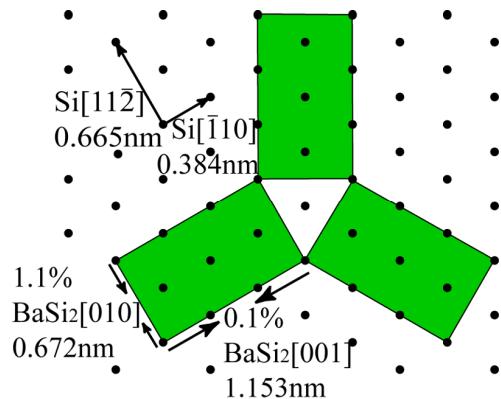
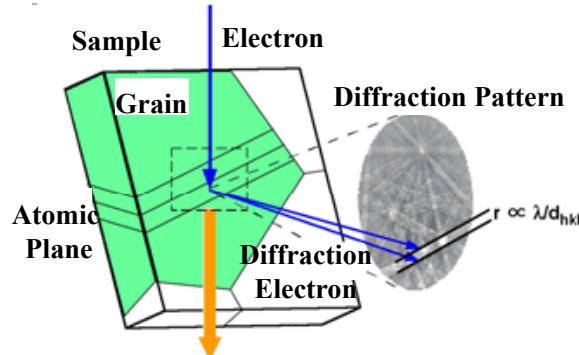
Photoresponse properties of BaSi₂ epitaxial films

Matsumoto, ..., Suemasu, *Appl. Phys. Express* **2** (2009) 021101.

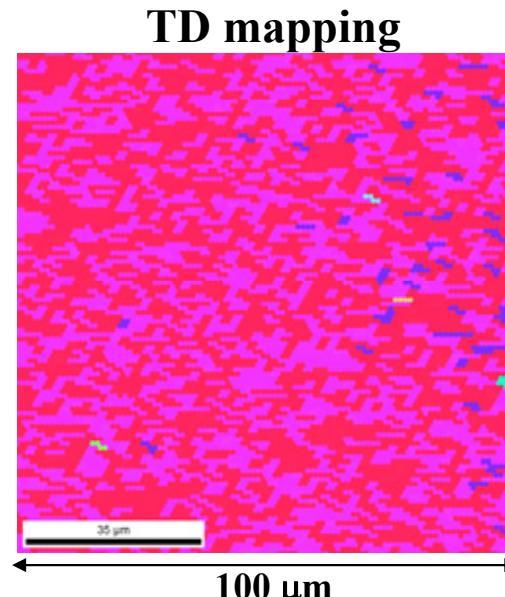
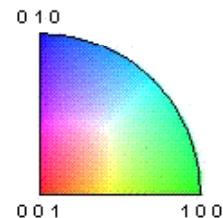


Analysis of grain size by Electron Backscatter Diffraction

Matsumoto,..,Suemasu, *Jpn. J. Appl. Phys.* (2010) in press.

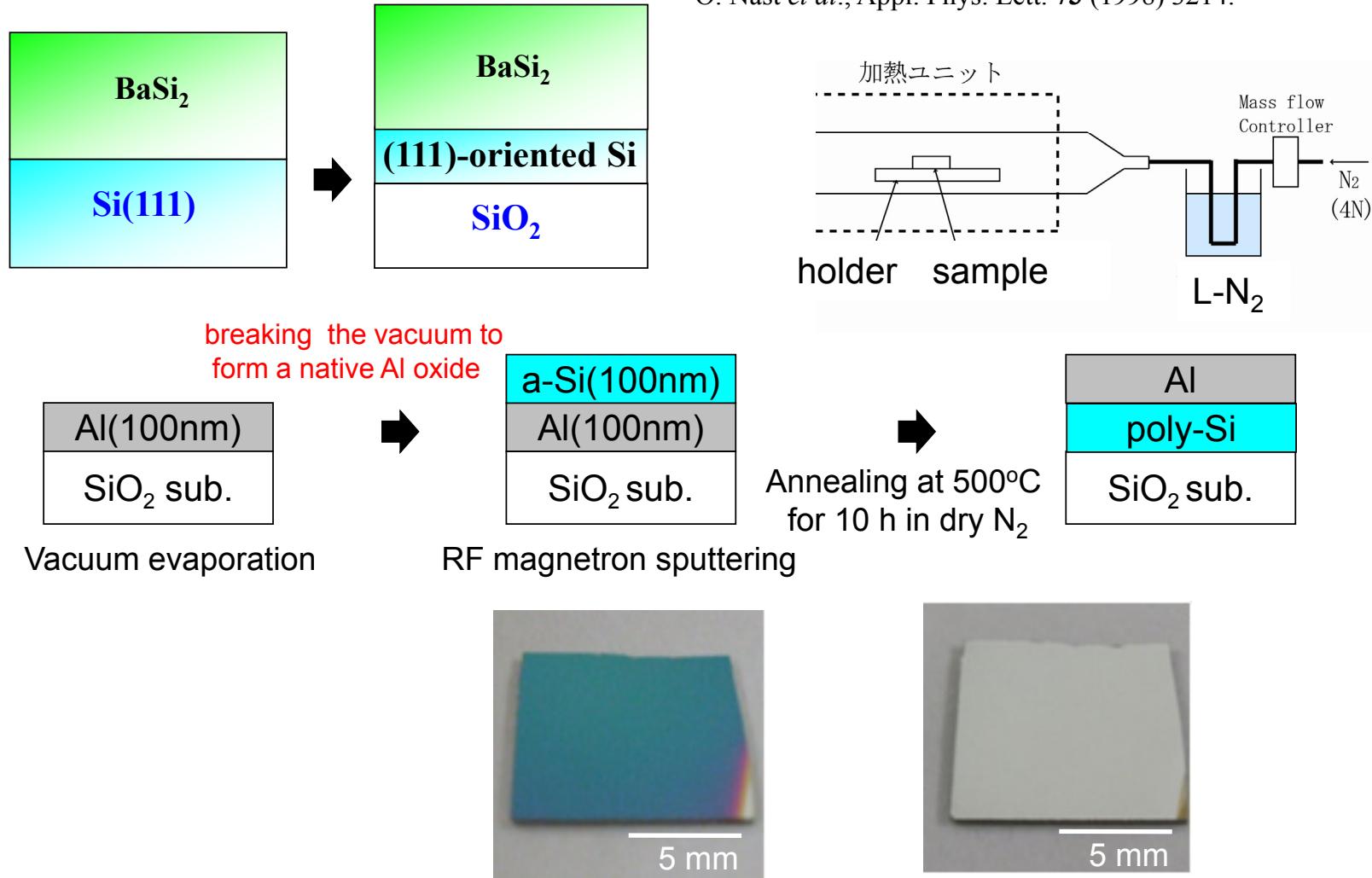


Grain size 3~10 μm



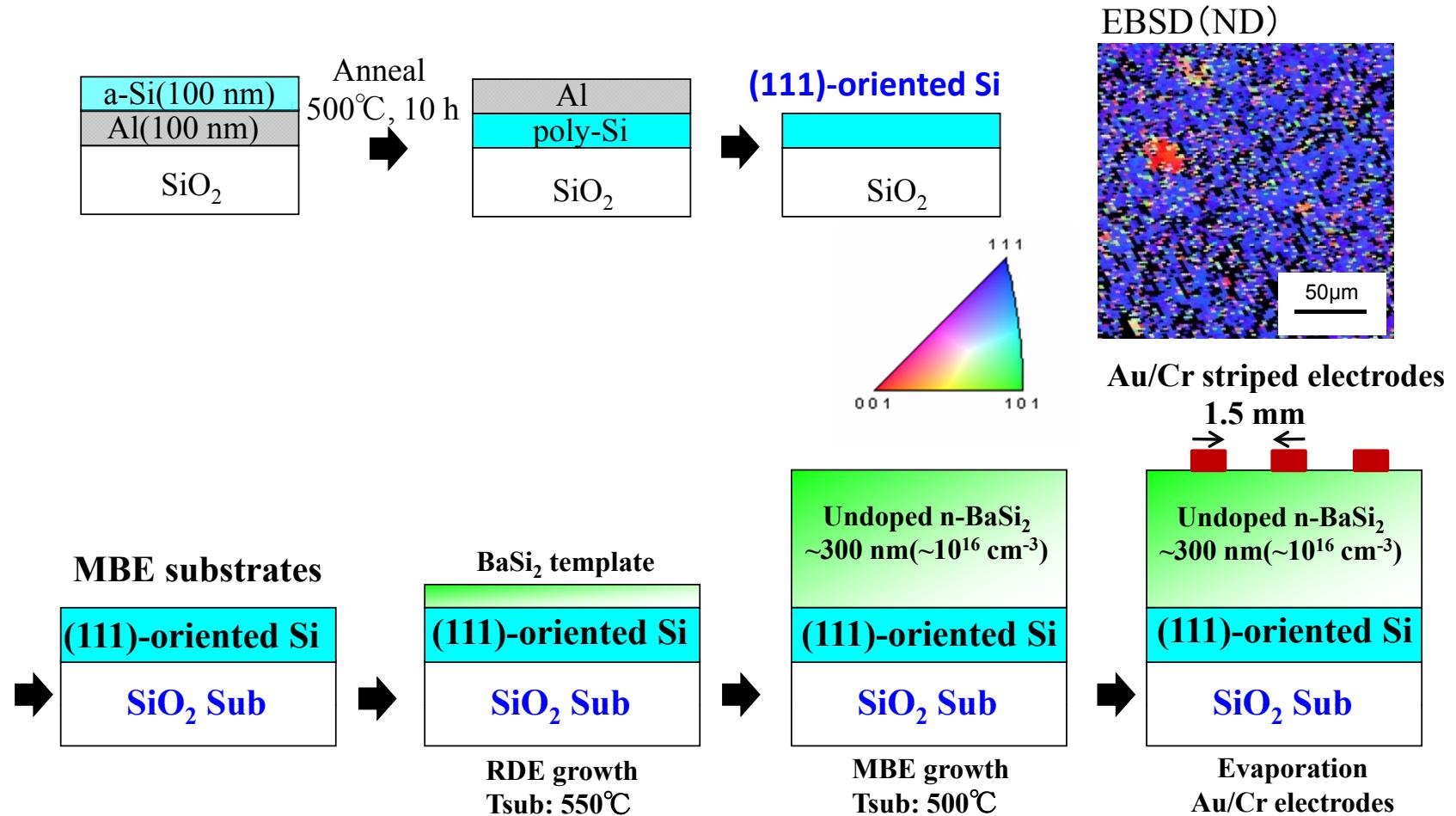
Formation of (111)-oriented Si layers on SiO_2 by Al-induced crystallization

O. Nast *et al.*, Appl. Phys. Lett. **73** (1998) 3214.



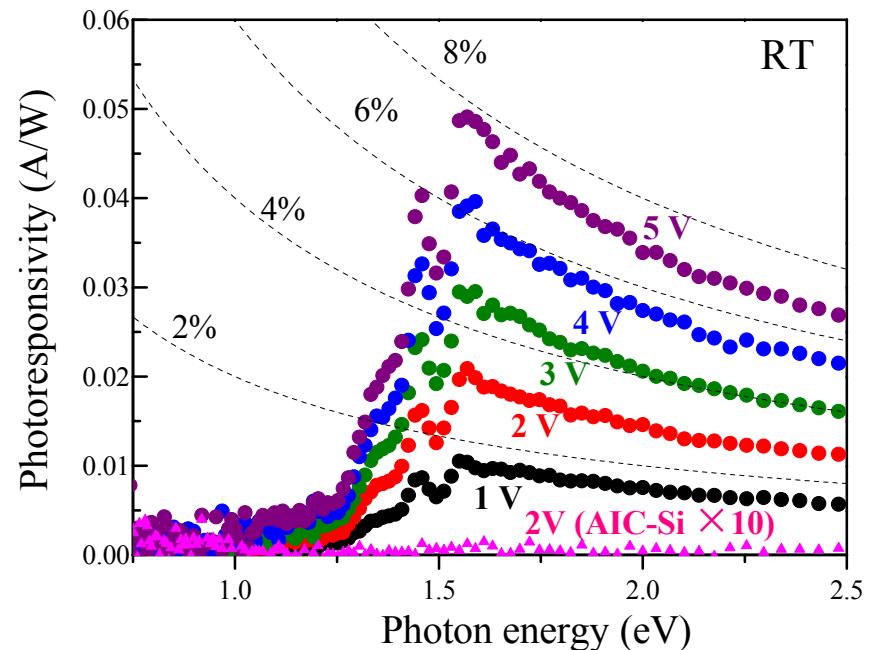
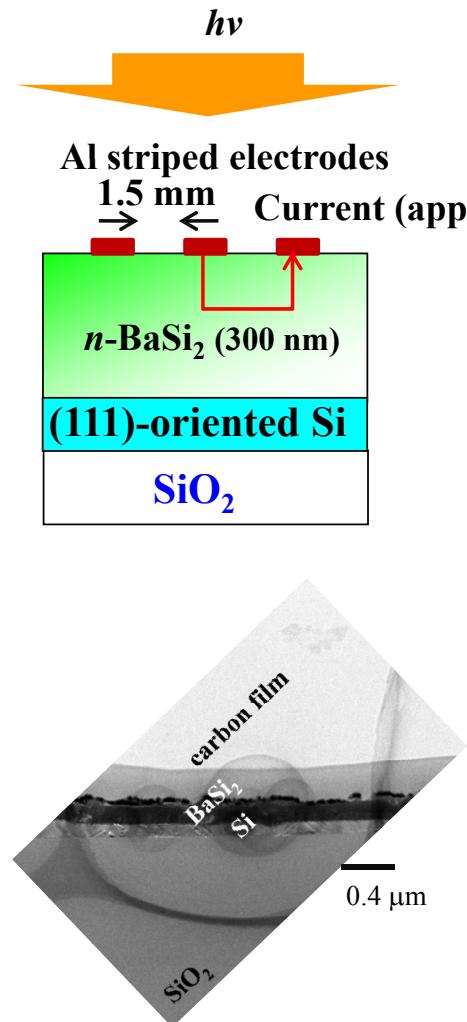
Growth of polycrystalline BaSi₂ films on AlC-Si/SiO₂

Tsukada,.....Suemasu, *J. Cryst. Growth* **311** (2009) 3581.



Photoresponse properties of polycrystalline BaSi₂ films on SiO₂

Tsukada,.....Suemasu, *Appl. Phys. Express* **2** (2009) 051601.



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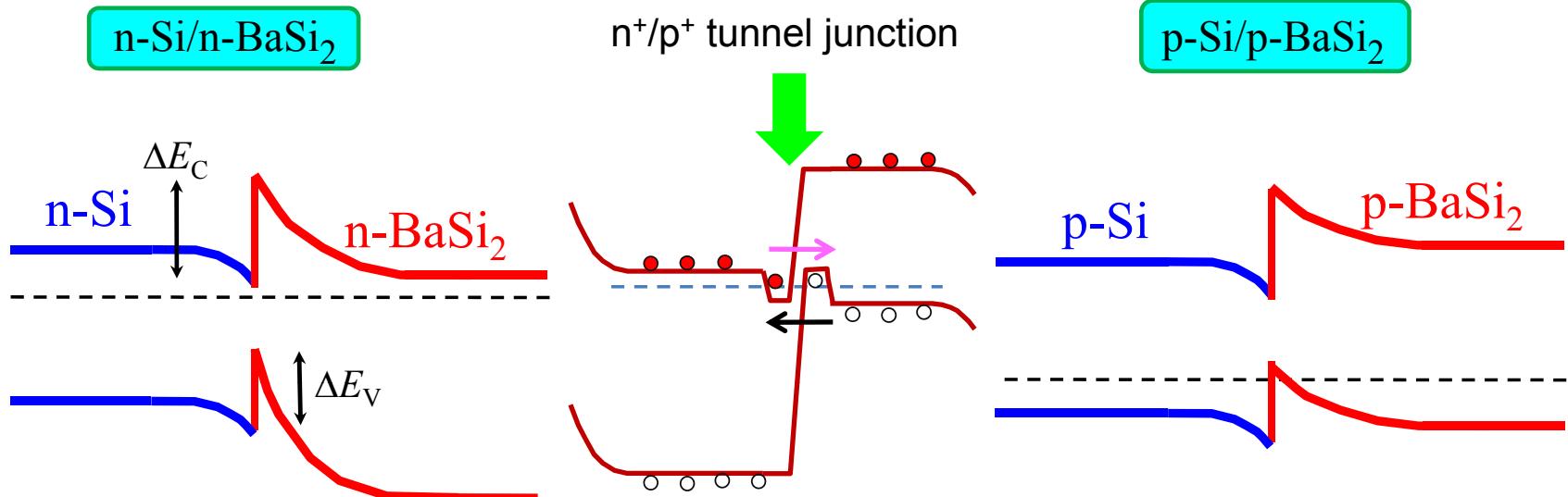
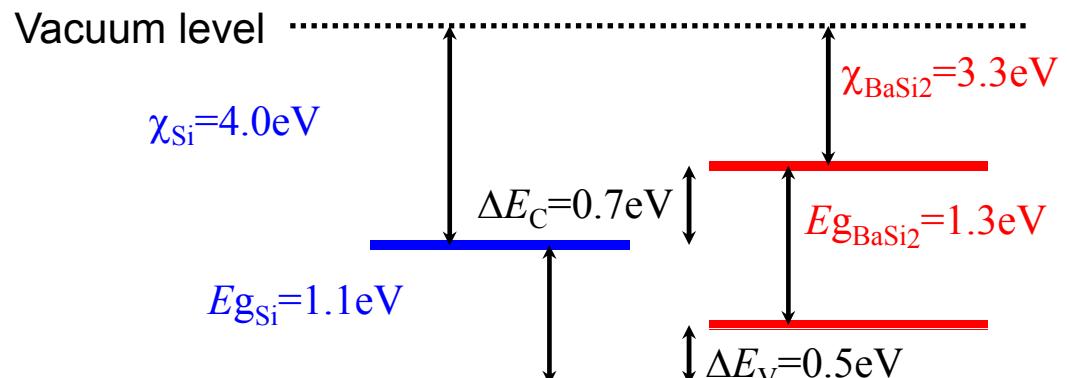
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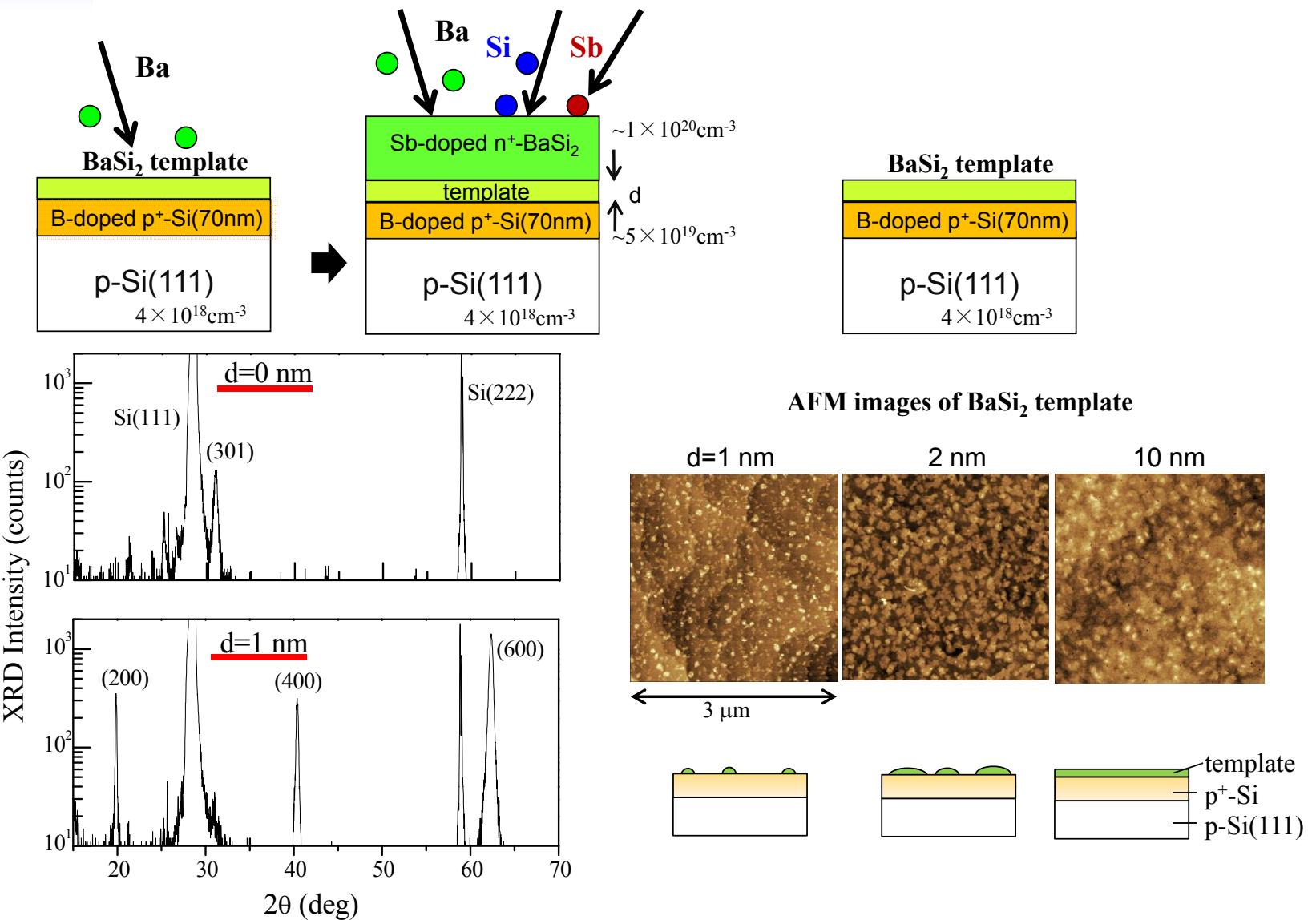
Demonstration of solar cell

Band diagrams of BaSi₂/Si structure

Suematsu et al., *Jpn. J. Appl. Phys.* **45** (2006) L519 .

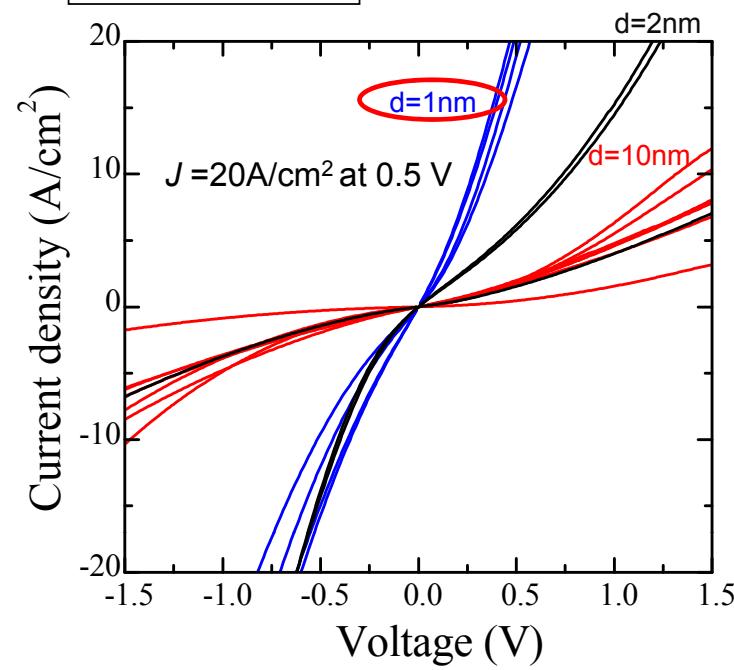
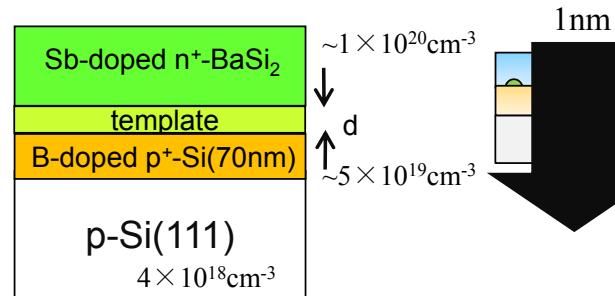


Formation of n⁺-BaSi₂/p⁺-Si tunnel junction by MBE

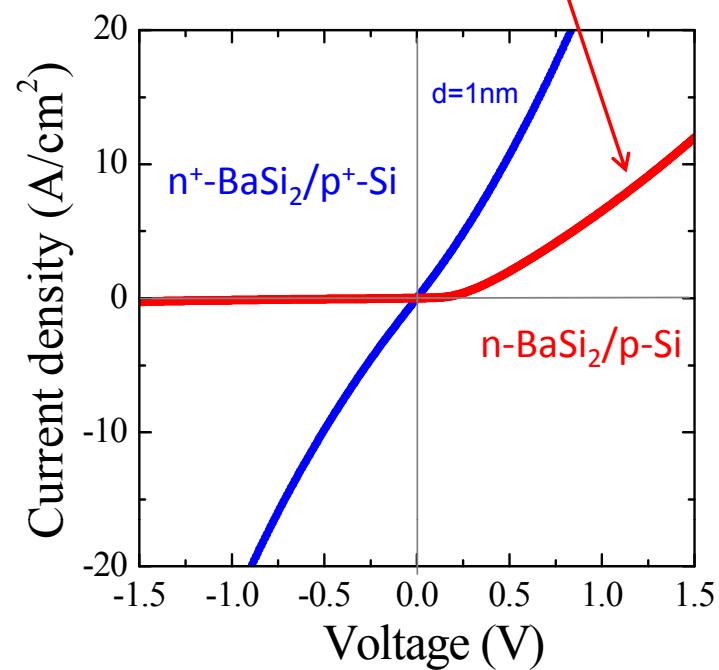
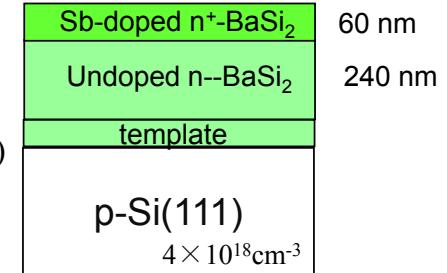


Dependence of $I-V$ characteristics on template layer thickness

$n^+-\text{BaSi}_2/\text{template}/p^+-\text{Si}$



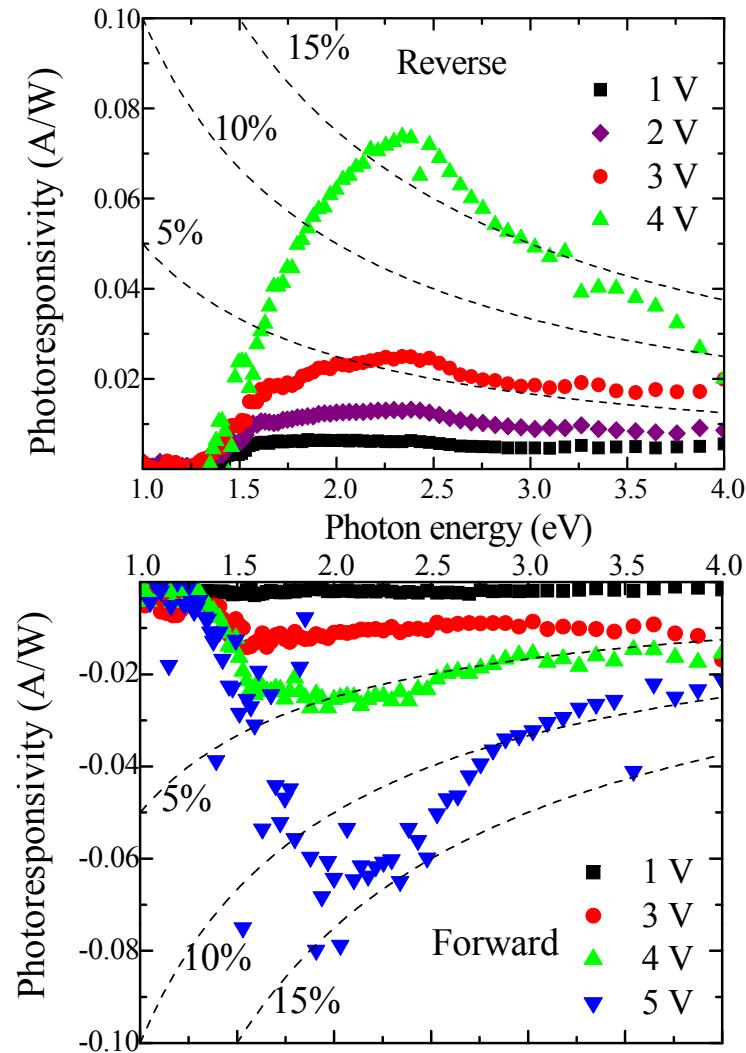
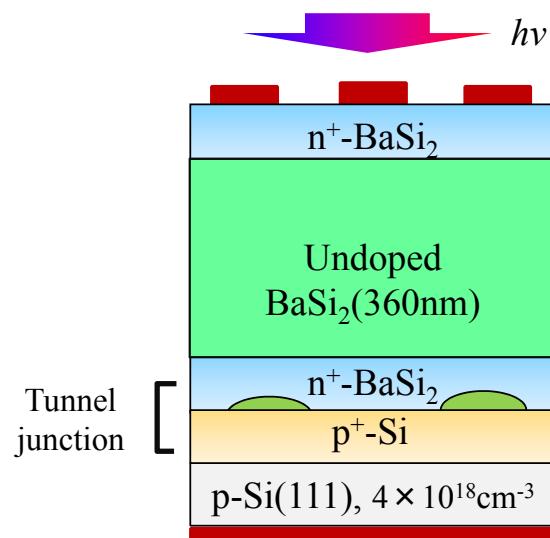
$n-\text{BaSi}_2/p-\text{Si}$



Photoresponsivity of BaSi₂ layers on tunnel junction

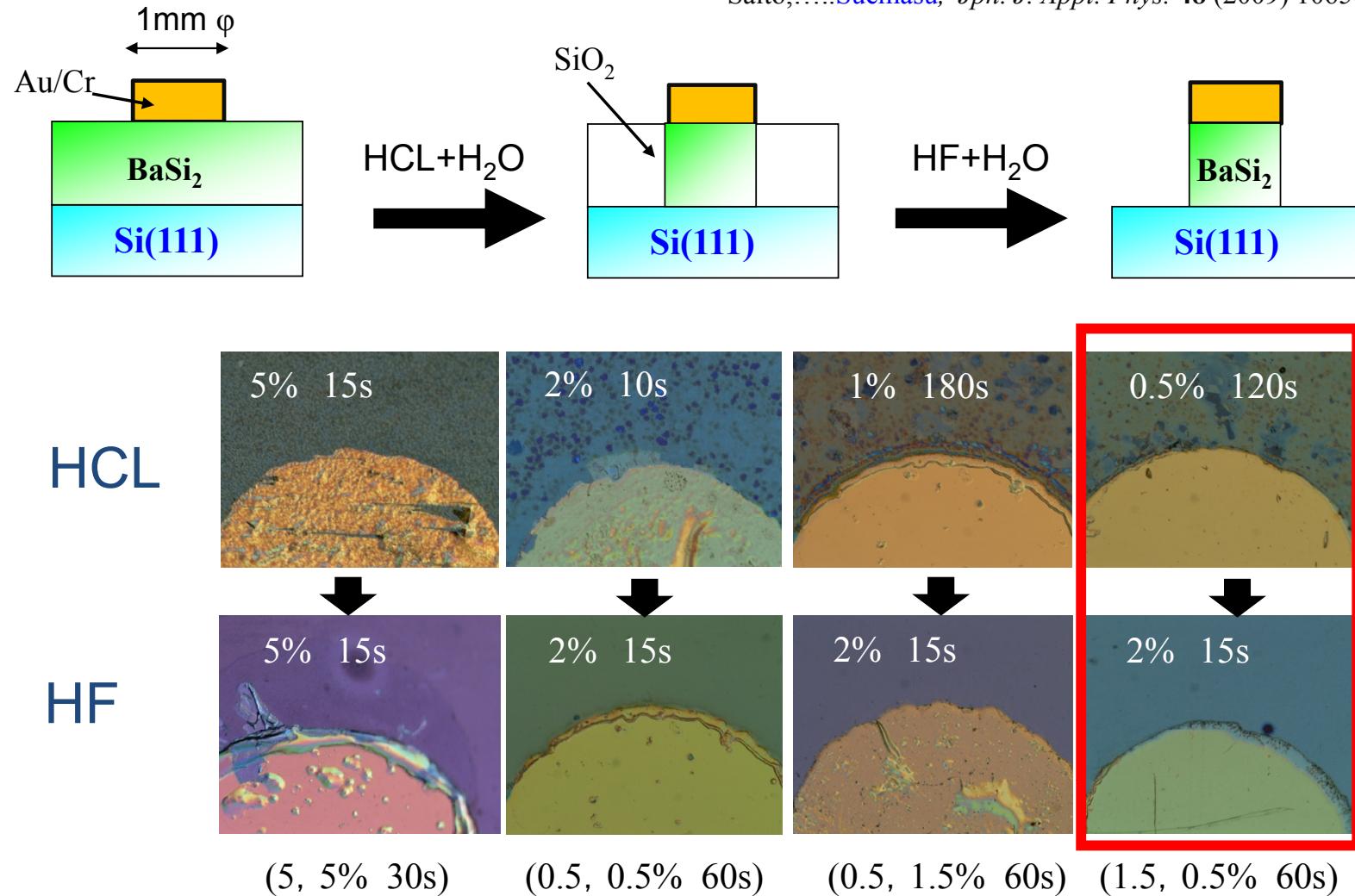
Saito,.....Suemasu, *Appl. Phys. Express* (2010) in press.

Current flow normal to the sample plane



Wet chemical etching of BaSi₂ layers on Si

Saito,.....Suemasu, *Jpn. J. Appl. Phys.* **48** (2009) 106507.



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特願2007-208729 , US2009/0044862

特願2008-218688 , PCT/WO2009/028560

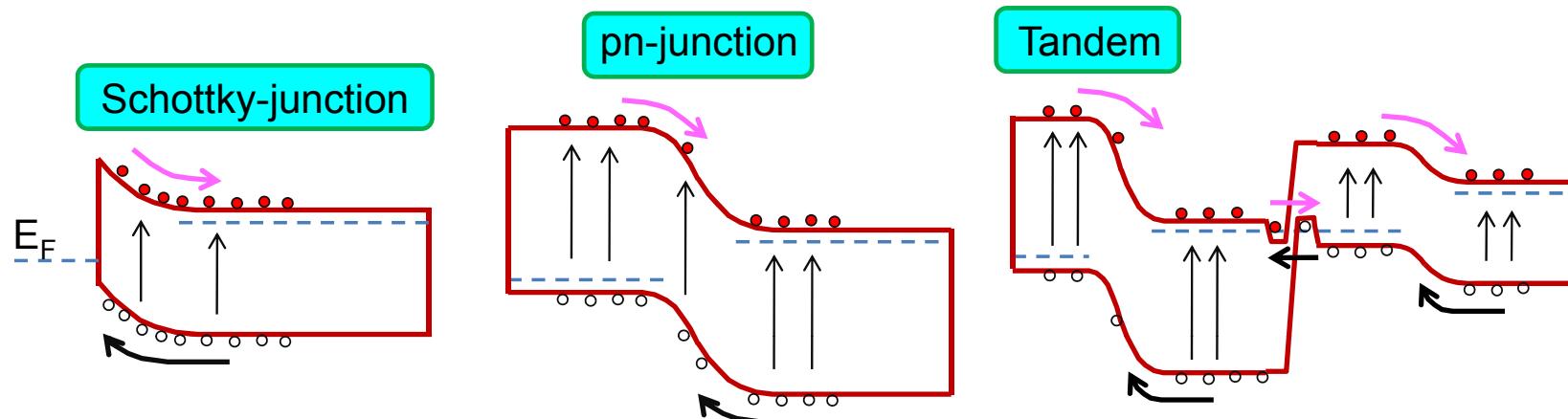
特願2009-115337,

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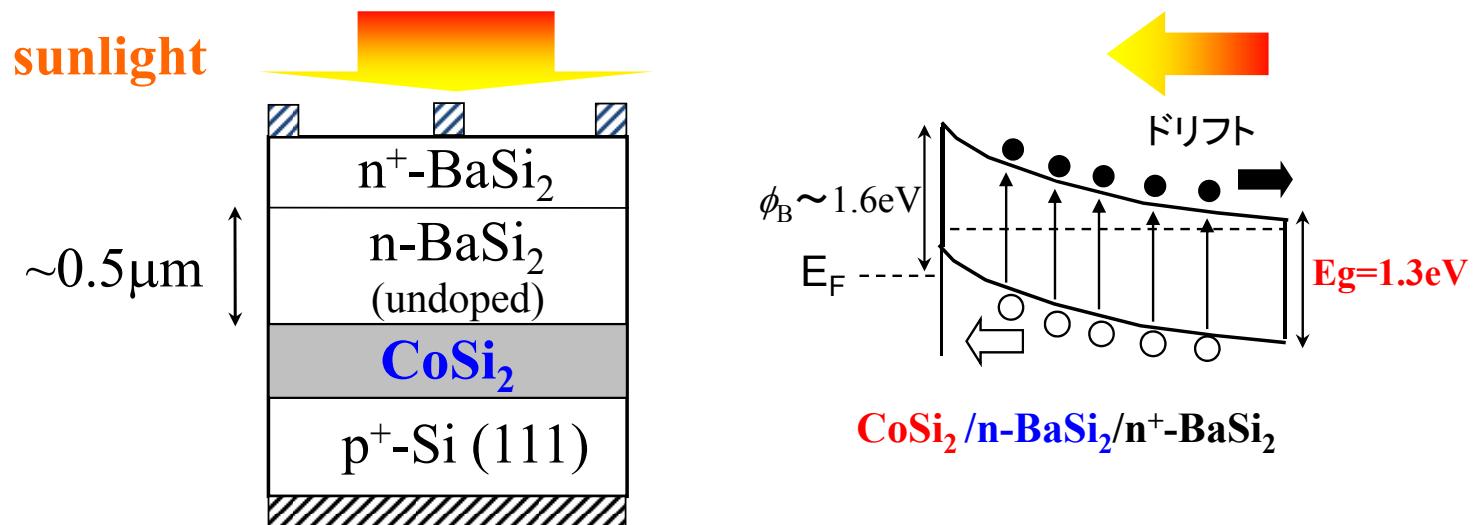
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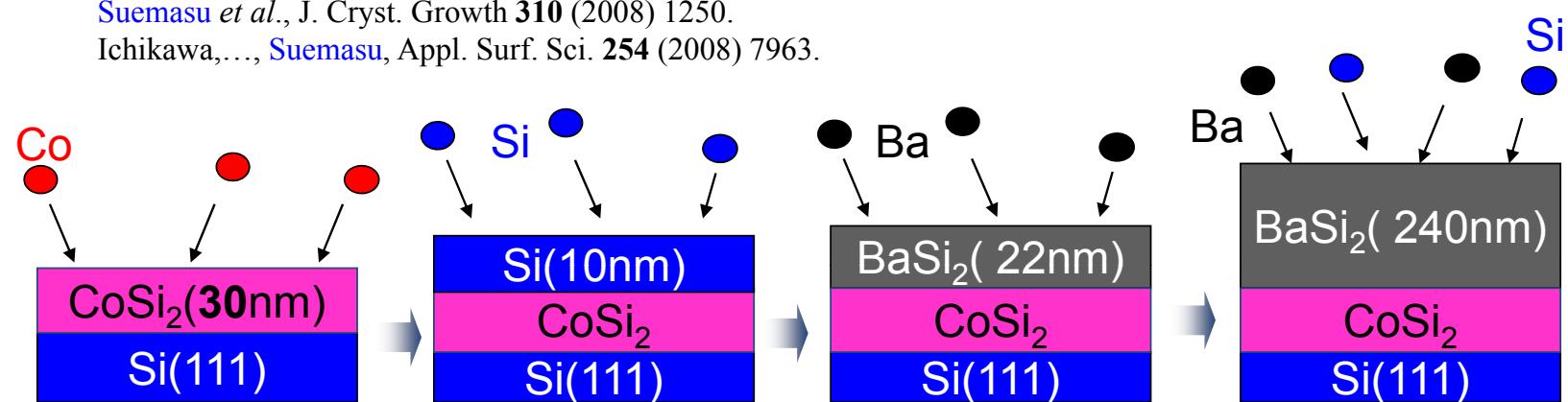
Schottky-barrier diode n-BaSi₂/CoSi₂



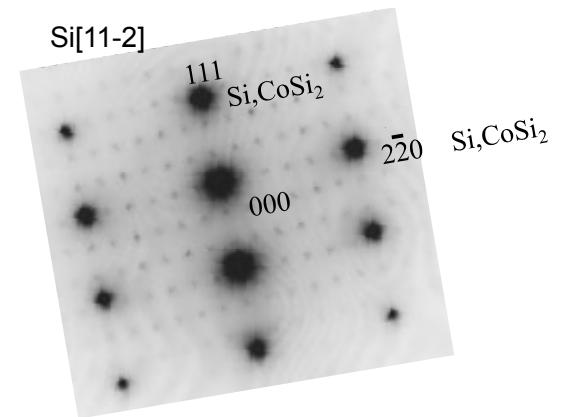
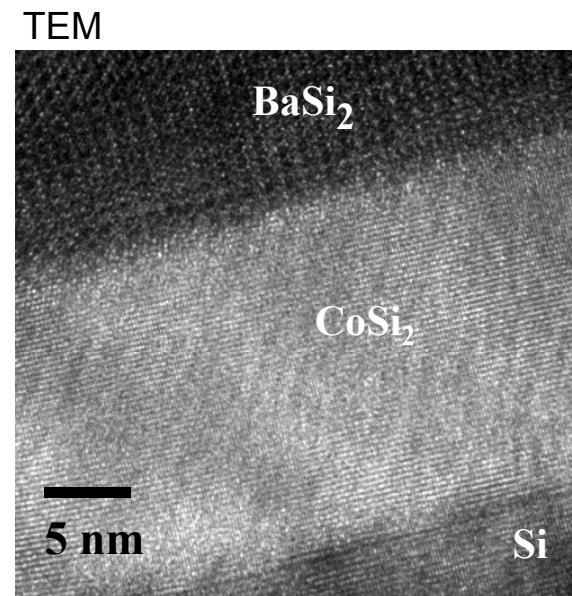
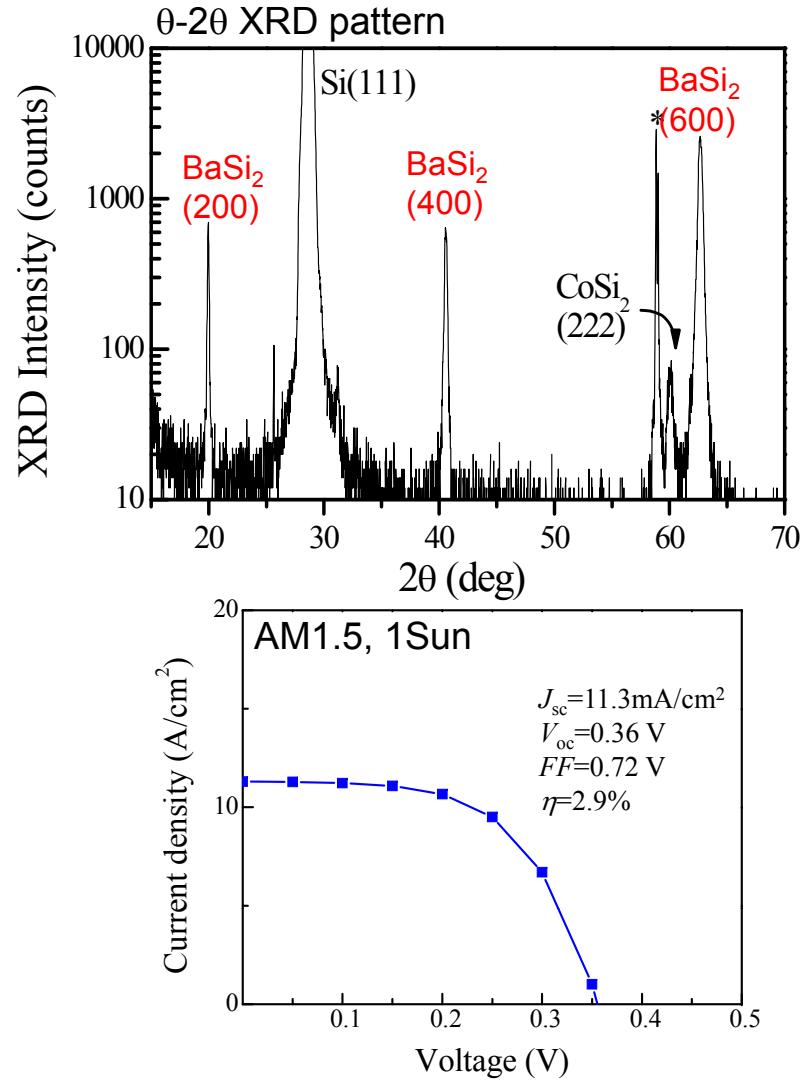
Epitaxial growth of BaSi₂/CoSi₂/Si(111) structure

Suematsu *et al.*, J. Cryst. Growth **310** (2008) 1250.

Ichikawa, ..., Suemasu, Appl. Surf. Sci. **254** (2008) 7963.



Characterization of n-BaSi₂/CoSi₂ Schottky diode



まとめ

① 不純物ドーピングによる伝導型、キャリア密度制御

Control of electron and hole concentrations by impurity doping

n-type: Sb($10^{16} \rightarrow 1 \times 10^{20} \text{cm}^{-3}$), As

p-type: In($10^{16} \rightarrow 5 \times 10^{17} \text{cm}^{-3}$), Al, Cu

② 分光感度特性

Photoresponsivity

Photocurrent increases sharply for photons greater than 1.25 eV ($\sim E_g$).

$R \sim 75 \text{mA/W}$ at 2.3 eV.

③ BaSi₂/Siトンネル接合の形成

Formation of heavily doped BaSi₂/Si tunnel junction for an electrical contact

$n^+ \text{-BaSi}_2/p^+ \text{-Si}, J = 21 \text{A/cm}^2$ at 0.5 V

④ Wet chemical etching

⑤ 太陽電池動作の実証

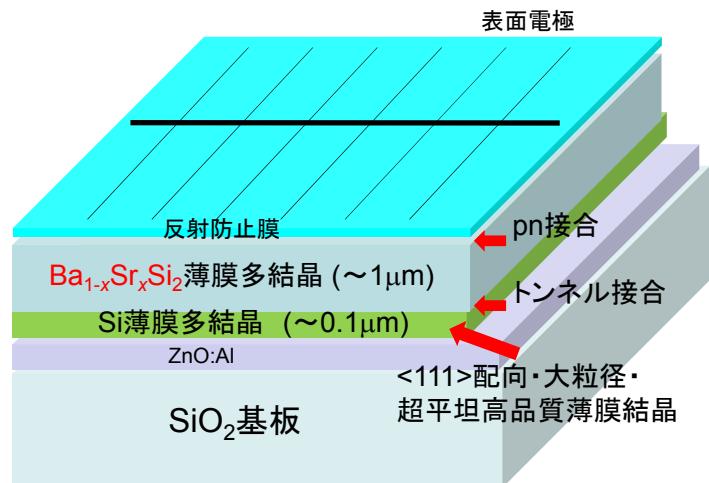
Demonstration of solar cell

Schottky-barrier diode

$\text{CoSi}_2/n\text{-BaSi}_2, \eta \sim 2\text{-}3\%$

今後の展開 Future plan

1. *pn* homojunction solar cell



2. *pn* heterojunction solar cell

