Materials related challenges en route to very high efficiency n-type silicon solar cells

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What are the lifetime requirement for high efficiency devices?

- Multi milliseconds lifetime for very high efficiency silicon solar cells
- What are the material related challenges to achieve high lifetime?

Modified from P. J. Cousins et al. 35th IEEE PVSC, (2010)
Outline

- Grown-in extended defects
- Characterizing as-grown defects
- Grown-in point defects in n-type CZ
- Grown-in point defects in n-type FZ
What grown-in defects are we looking at?

Vacancy  Foreign interstitial  Stacking Fault  Precipitate

Silicon interstitial  Dislocation  Void  
(COP, FPD, D-defects)

Modified from F. Shimura, "Semiconductor silicon crystal technology" (1989)
Effect of growth rate on defect types

Voronkov criteria v/G

Cross section of a wafer with vacancy rich and interstitial rich silicon

- V: growth rate
- G: axial temperature gradient
  - High V/G (fast pulling rate): Vacancy mode
  - Low V/G (slow pulling rate): Interstitial mode
  - Intermediate V/G: P (Particle) band, H (High vacancy) band, L (low vacancy) band

Y. Hu et al 26 EUPVSEC (2011)
Effect of growth rate on defect distribution

Oxygen precipitates


Modified from F. Shimura, "Semiconductor silicon crystal technology" (1989)
Oxygen precipitates and high temperature processing

Increased precipitate density

Strained precipitates

Metallic decoration

Clean cell process
Non-clean cell process


J. Haunschild et al. phys. stat. sol. RRL (2011)
Oxygen precipitates

- M. Forster et al. N-PV workshop (2014)
Stacking faults

Modified from F. Shimura, "Semiconductor silicon crystal technology" (1989)


Stacking faults


Dislocations

Modified from F. Shimura, "Semiconductor silicon crystal technology" (1989)


B. Hallam et al. IEEE JPV (2014)
Dislocations


B. Hallam et al. IEEE JPV (2014)

Grown-in and process-induced **extended** defects

**Oxygen precipitates**

**Stacking faults**

**Dislocations**

Modified from F. Shimura, "Semiconductor silicon crystal technology" (1989)
Grown-in and process-induced **extended** defects

**Oxygen precipitates**


**Stacking faults**


**Dislocations**

- B. Hallam et al. IEEE JPV (2014)
- M. Forster et al. N-PV workshop (2014)
Material-related challenges en route to high efficiency n-type solar cells
What are the defects between us and the Intrinsic lifetime?

Material-related challenges en route to high efficiency n-type solar cells

![Graph showing efficiency (%)](image)

**Challenges for mono n-type cells**
- Intrinsic point defects paired with light elements?
- Extended defects (disl, OSF...)
- VOₓ, VHₓ, VNₓ...
- Metals (Cr, Zn...)?
Grown-in and process-induced point defects

Thermal donors

Modified from F. Shimura, "Semiconductor silicon crystal technology" (1989)

N. Najid et al. N-PV workshop (2013)

Grown-in and process-induced point defects


...  ...

Scarce literature on the influence of intrinsic point defects on the lifetime

Modified from F. Shimura, "Semiconductor silicon crystal technology" (1989)

N. Najid et al. N-PV workshop (2013)

Outline

• Grown-in extended defects
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Let's have a small exercise

- Lifetime of 1ms
- Assume a midgap defect with a standard capture cross section of $\sigma_p = \sigma_n = 1 \times 10^{-14}$ cm$^2$

$$\tau_{p0} = \frac{1}{N_t \sigma_p v_{th}}$$
Let’s have a small exercise

- Lifetime of 1 ms
- Assume a midgap defect with a standard capture cross section of $\sigma_p = \sigma_n = 1 \times 10^{-14} \text{ cm}^2$
  
\[
\tau_{p0} = \frac{1}{N_i \sigma_p v_{th}}
\]
- Defect density $N = 1 \times 10^{10} \text{ cm}^{-3}$
- Cannot be identified with DLTS or EPR
- We need lifetime spectroscopy to identify the defect
Influence of passivation

• Using SiN$_X$:H or Al$_2$O$_3$:H can potentially anneal or hydrogenate bulk grown-in defects

• We need room temperature passivation

• We use a range of passivation techniques to understand hydrogenation effects
HF passivation to investigate grown-in defects

HF passivation provides room temperature passivation

Value in understanding defect in their as-grown or as-processed state

- Represent the “true” growth conditions
  - Using thermal SiO$_2$, SiN$_X$:H or Al$_2$O$_3$:H can change the state of the defect
  - HF passivation will measure the defect as is
  - $S_{\text{eff}} = 1.1 \pm 0.2$ cm.s$^{-1}$

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Defects in CZ silicon

- Anneal at 360°C for different length of time
- The defect is deactivated after 30 min
Defects in CZ silicon

(a) After 450°C anneal
(b) After 550°C anneal
(c) After 650°C anneal

Before 450°C anneal
Before 550°C anneal
Before 650°C anneal

CZ sample C
CZ sample B
CZ sample A

$\Delta p$ ($\text{cm}^{-3}$) $\tau$ ($\mu$s)
Defect thermal de-activation

- Isochronal anneal for 30 min
- The defect is deactivated above 360°C
Identification (tentative) of the defect

- The defect is deactivated above 360°C
- The defect could be related to vacancy-oxygen pairs
- Highly influential for heterojunction designs
Defects in CZ silicon

- Oxygen is a problem for precipitates, stacking faults, thermal donors and pairing with vacancies
- Why not use FZ silicon?
Outline

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Why is there nitrogen in FZ silicon?

- Mitigates the impact of extended defects.
- Suppresses the formation of vacancy and interstitial aggregates
  \[ \text{N}_2 + \text{V} \rightarrow \text{N}_2\text{V} \]
  \[ \text{N}_2\text{V} + \text{I} \rightarrow \text{N}_2 \]
- Pins dislocations for improved mechanical stability at high temperature
Defects in nitrogen-doped FZ silicon?

- Nitrogen-doped FZ silicon wafers have lower as-grown lifetime than nitrogen-lean FZ or CZ wafers
Thermal deactivation of defect

- Lifetime increases significantly after anneal at 1000°C
- Removal or transformation of recombination active defect
- What is the defect?
Spatial distribution of the lifetime $\text{Al}_2\text{O}_3:\text{H}$

- Higher lifetime around the edges
- Radially symmetric distribution of lifetime
Spatial distribution of the defect lifetime

\( \text{SiN}_x:\text{H} \)

- Higher lifetime around the edges
- Radially symmetric distribution of lifetime
- Higher lifetime than \( \text{Al}_2\text{O}_3:\text{H} \)
- What does that imply for the defect structure?
Spatial distribution of the defect

- Defect density higher in the centre
- Nitrogen constant laterally
- Radial distribution suggests nitrogen-vacancy point defect
- Is there one or many different defect species?
One or many defect species?

- Absence of a single linear trend
- More than one type of defect

\[ \tau_p = \frac{1}{\alpha_{pN}} \left[ 1 + \frac{n_1}{n_0} + \frac{p_1}{n_0Q} + Y \left( \frac{1}{Q} - \frac{n_1}{n_0} - \frac{p_1}{Qn_0} \right) \right] \]

Effect of passivating films with different hydrogen contents

- SiN$_X$:H contains 15%-20% total H (complexed and atomic)
- Al$_2$O$_3$ contains less than 5% total H
- Increases the lifetime through bulk hydrogenation
Conclusion: Extended defects

• Stacking faults and oxygen precipitates can severely limit the lifetime of n-type monocrystalline silicon
• High temperature processes can increase the recombination activity by changing the precipitate density, having strained precipitates and through metallic decorations
• Dislocations and slip lines are detrimental but should not occur when using high purity feedstocks
Conclusion: Point defects

- We demonstrate that intrinsic point defects paired with light elements can limit the lifetime of high purity silicon wafers.

- $V_XO_Y$ and $V_XN_Y$ complexes are two likely candidate limiting the lifetime of CZ and FZ silicon.

- Solutions to increase the lifetime:
  - from 1-2ms to 5ms after annealing above 360°C of CZ silicon.
  - from 0.5 ms to 3-5ms after annealing above 1000°C or hydrogenation of FZ silicon.
What is a control wafer?

- Standard high temperature and passivation processes are likely to affect the states or concentrations of defects through hydrogenation or annealing.
- There is no such things as a perfect and stable control.
- One must use multiple controls in order to rightfully interpret enhanced surface passivation or cell parameters.
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Thank you for your attention