Impact of hydrogen peroxide in ultrapure water

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Outline

1. Introduction

2. Experimental approach to assess the impact of H_2O_2 on SiGe epitaxial sequence using Si(100) wafers

3. Investigation of mechanism
   (1)Experiments to assess the H_2O_2 impact using Si(111) surface
   (2)Discussion

4. Summary

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H_2O_2 in ultrapure water (UPW)

Table. Impurities in General UPW

Impurities	Concentration
Particles	≦0.1 Pcs/mL
Organics	≦1.0 μg/L
Critical metals	≦0.0001 μg/L
Dissolved oxygen	≦1.0 μg/L
H2O2	5 to 25 μg/L

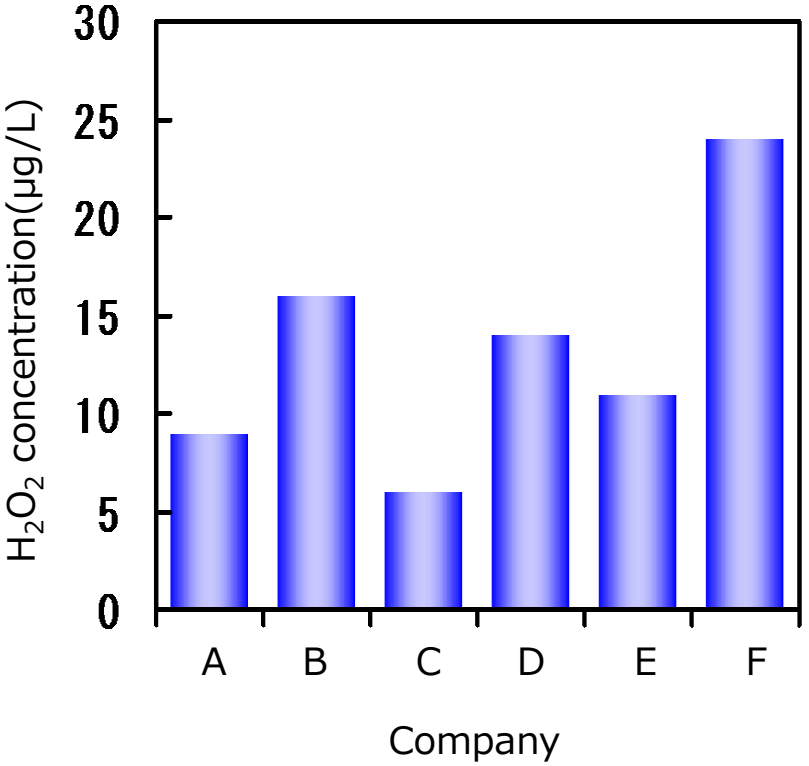

Fig. H_2O_2 concentration in UPW at a customer's Fab

H_2O_2 ,that is stronger oxidizer, exists in UPW and its concentration is ten times higher than these of other impurities

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Historical transition of the H_2O_2 issue in UPW

Year	Contents
2003	The first report, that mentioned the presence of H_2O_2 in UPW due to UV oxidation process was issued. [1)]
2007	H_2O_2 decomposition catalyst for UPW was reported. [2)]
2013	H_2O_2 in-line monitor for UPW was reported. [3)]
2016	Item of H_2O_2 concentration was added to ITRS 2.0. [4)]

<Reference>

1) Abe et al, *"The deterioration of Ultrapure Water Quality Under the Influence of Hydrogen Peroxide"*, Journal of Ion Exchange,Vol 14,p.273~276, July 2003

2) Kobayashi et al, *"Removal of Hydroxy Peroxide in an Ultra Pure Water System"*, The 54th JSAP Autumn meeting, 2007

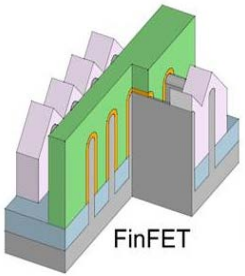
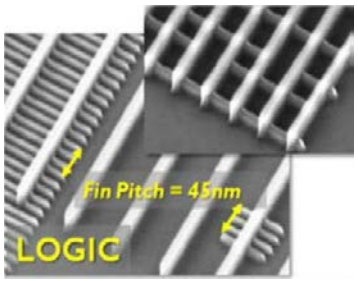
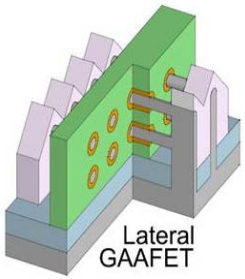
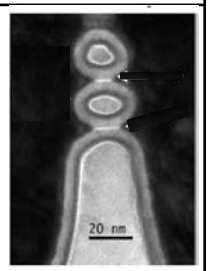
3) Miyazaki et al, *"Advanced Hydrogen Peroxide Removal Technology Using Nano-sized Pt Particle Catalyst on Anion Exchange Resin"*, UPWMicro2013

4) Libman et al, *"UPW ITRS and SEMI: Synergy of Enabling Advanced Existing and Future Technologies"*, UPWMicro 2015

The issue of H_2O_2 has been widely known since more than ten years ago.

Details of the target cleaning process

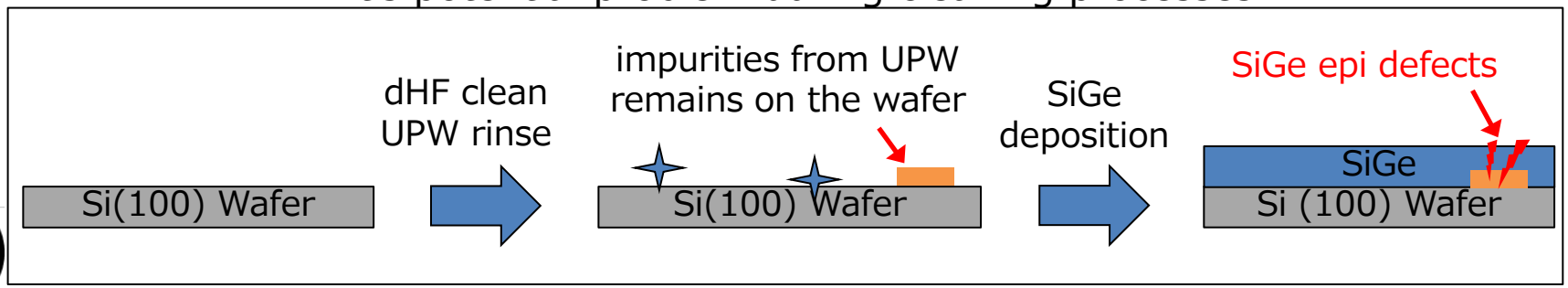
Logic semiconductor roadmap from imec

Year	2013	2014	2015	2016	2017	2018	2019	2020
Node (nm)	20～14			10			7	
Channel Material	Si			**Si, SiGe**			**Si, SiGe(Ge)**	
Structure							 	

Metal gate | Silicon | S/D epi
Gate oxide | Isolation | W electode

[Ref.: Yakimets D. et al., IEEE TRANSACTIONS ON ELECTRON DEVICES, VOL. 62, NO. 5, MAY 2015]

SiGe epitaxial process on semiconductor and it's potential problem during cleaning processes



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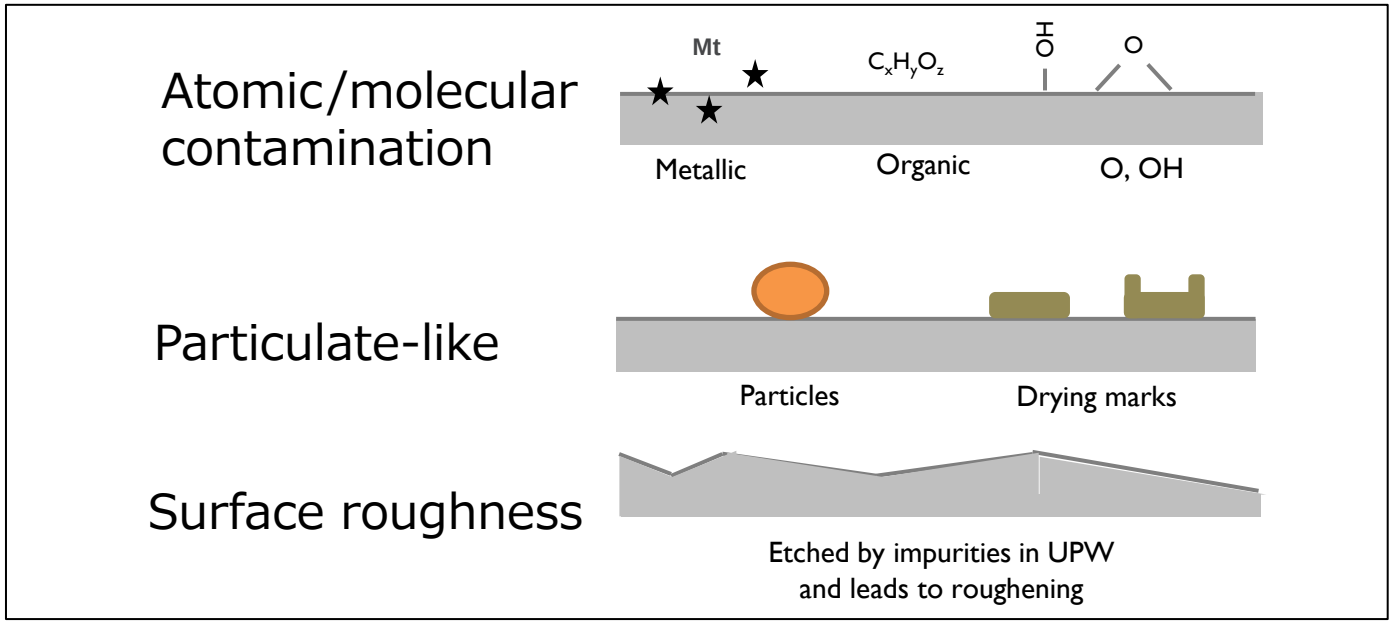
Purpose of this study

Typical impact of impurities in UPW on a wafer during wet cleaning processes



The impact of the dilute H_2O_2 in UPW on cleaning processes is unclear.

Evaluate the impact of the dilute H_2O_2 in the UPW using cleaning tools.

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Experimental method using single wafer cleaning tool

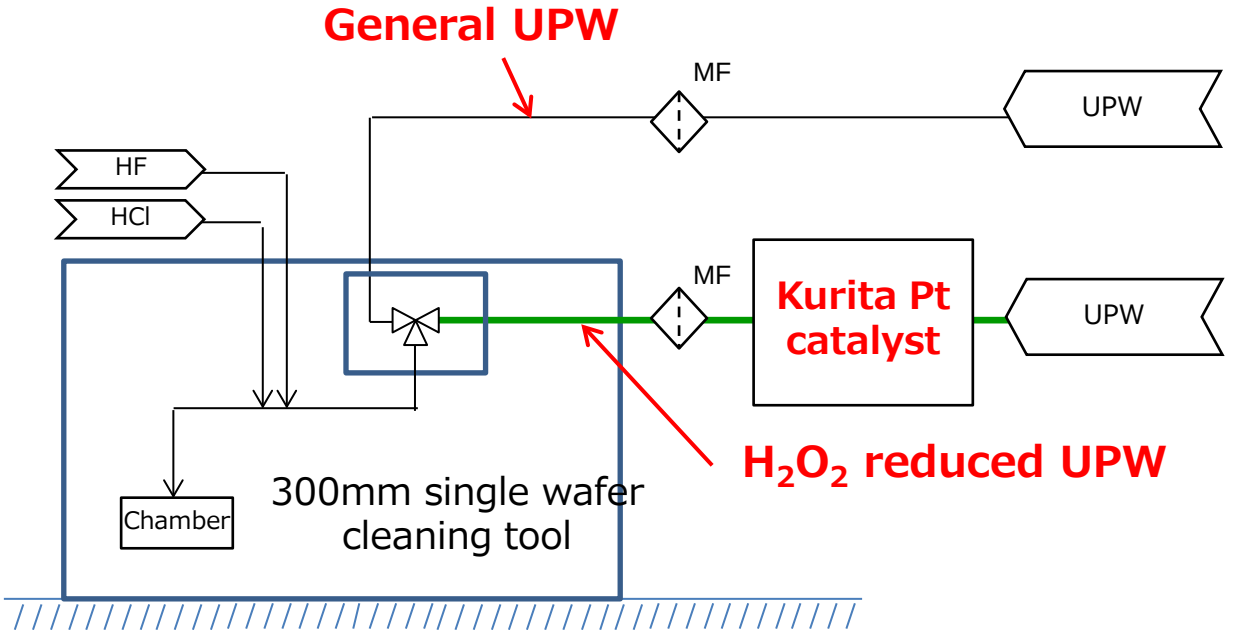


Fig: Single wafer cleaning tool

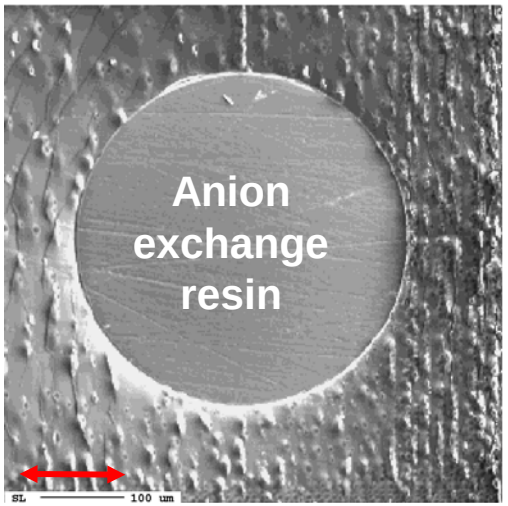
Table: H_2O_2 concentration in the UPW

General UPW	H_2O_2 reduced UPW (with Kurita Pt catalyst)
8-10 μg/L	<1 μg/L

A split test was conducted to clarify the impact of the dilute H_2O_2 during the SiGe pre-epi cleaning process using either H_2O_2 reduced UPW or general UPW.

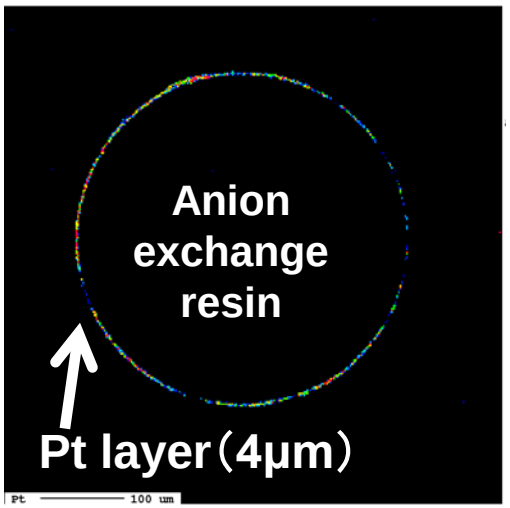
Feature of Kurita Pt catalyst <Decomposition>

SEM (cross-section Pt-resin)



100μm

EDS (cross-section Pt-resin)



Spherically shaped anion exchange resin coated with Pt layer

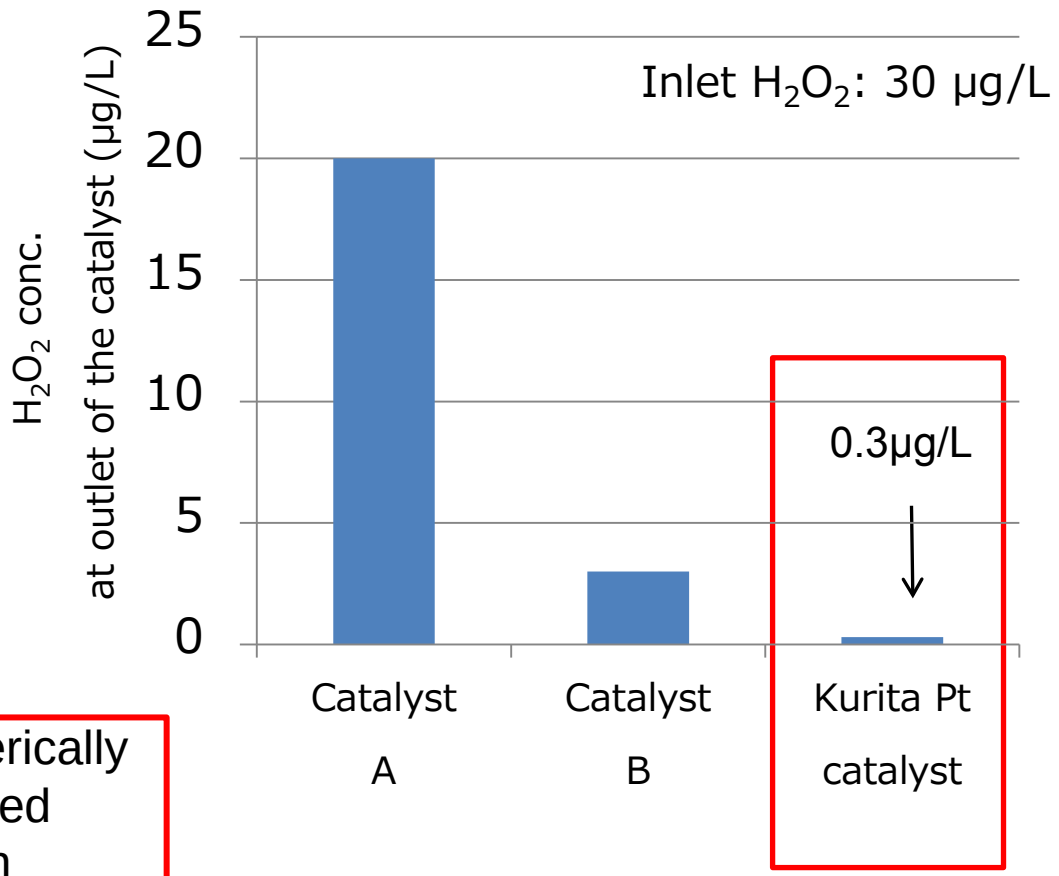


Fig. Decomposition performance compared with other catalysts

Kurita Pt catalyst decomposes H_2O_2 in UPW to less than 1 μg/L.

Feature of Kurita Pt catalyst <Elution>

Table Elution amount from catalyst

Metal	Units	Kurita Pt catalyst	Catalyst B
Fe	ng/L	<0.1	<5
Cu		<0.1	<5
Al		<0.1	<5
Ni		<0.1	<5
Mn		<0.1	<5
Co		<0.1	<5
Ca		<0.1	<5
Zn		<0.1	<5
Mg		<0.1	<5
Li		<0.1	<5
K		<0.1	<5
Na		**<0.1**	**10**
Pd		**<0.1**	**8**
Pt		**<0.1**	<5

Condition
Amount : 200ml-R
SV : 300 1/hr

- Kurita Pt catalyst has less metal elution.

Feature of Kurita Pt catalyst <Application>

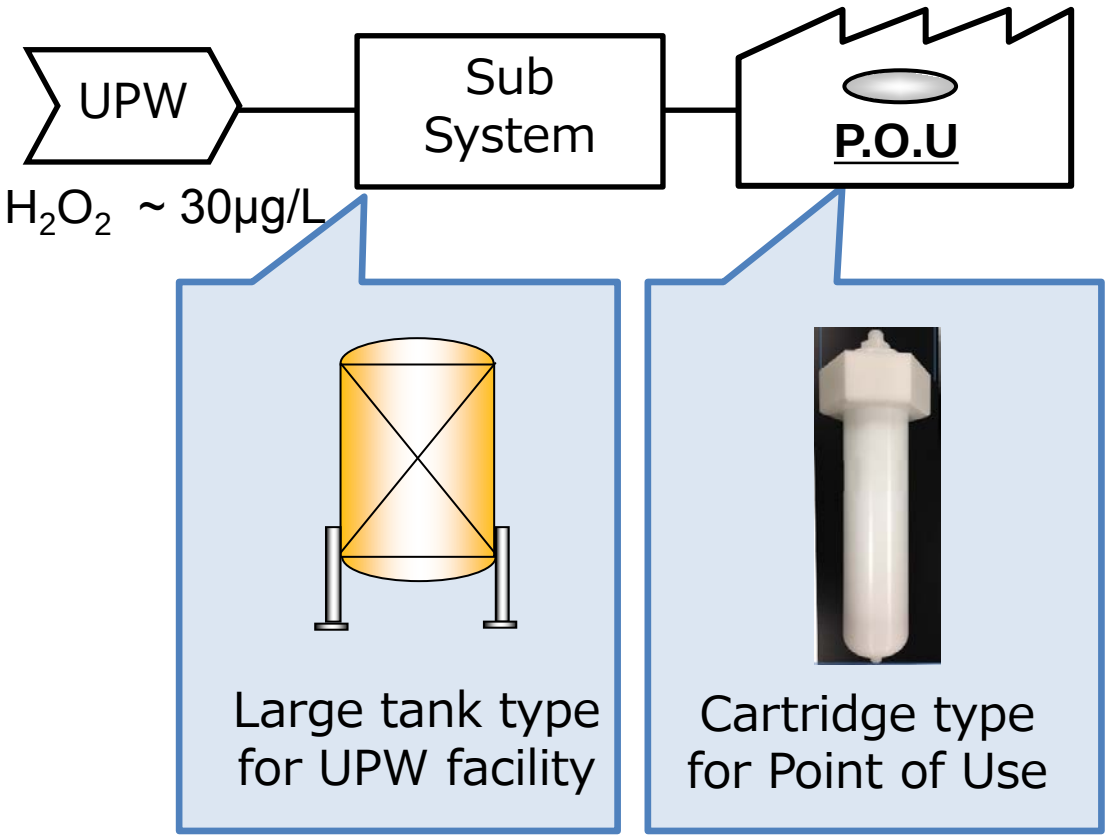


Fig Scope of application

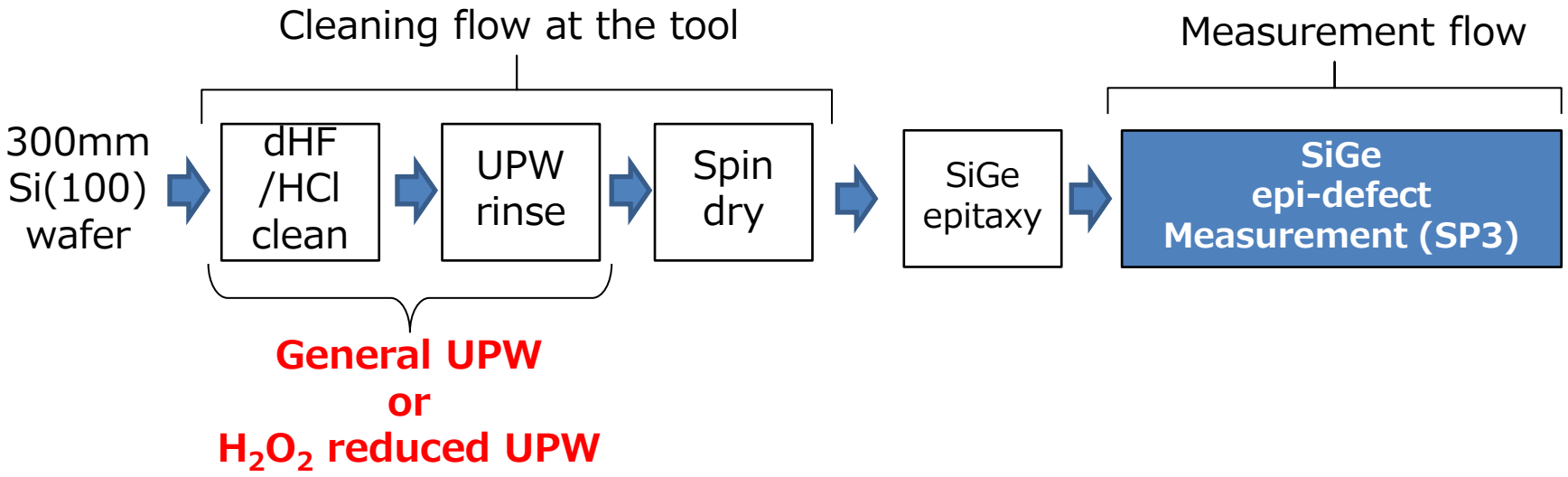
Table performance of commercially installed Kurita Pt catalyst

	Number of years keeping H_2O_2 below 1μg/L
Fab A	8 years
Fab B	6 years
Fab C	4 years
Fab D	3 years

and so on・・・

Kurita Pt catalyst has a lot of installation records in semiconductor Fabs.

Process flow of experimental apparatus for SiGe epitaxial sequence



Contents	Condition
Wet cleaning	HF 0.7% clean diluted with General UPW or H_2O_2 reduced UPW
SiGe epi-defects measurement	- After wet clean, 80nm $Si_{0.8}Ge_{0.2}$ layer was epitaxially grown by an epi tool. - KLA-T Surfscan SP3 was used, [K. Wostyn et al ECS Trans (2014)]

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Result: SiGe epi-quality measurement

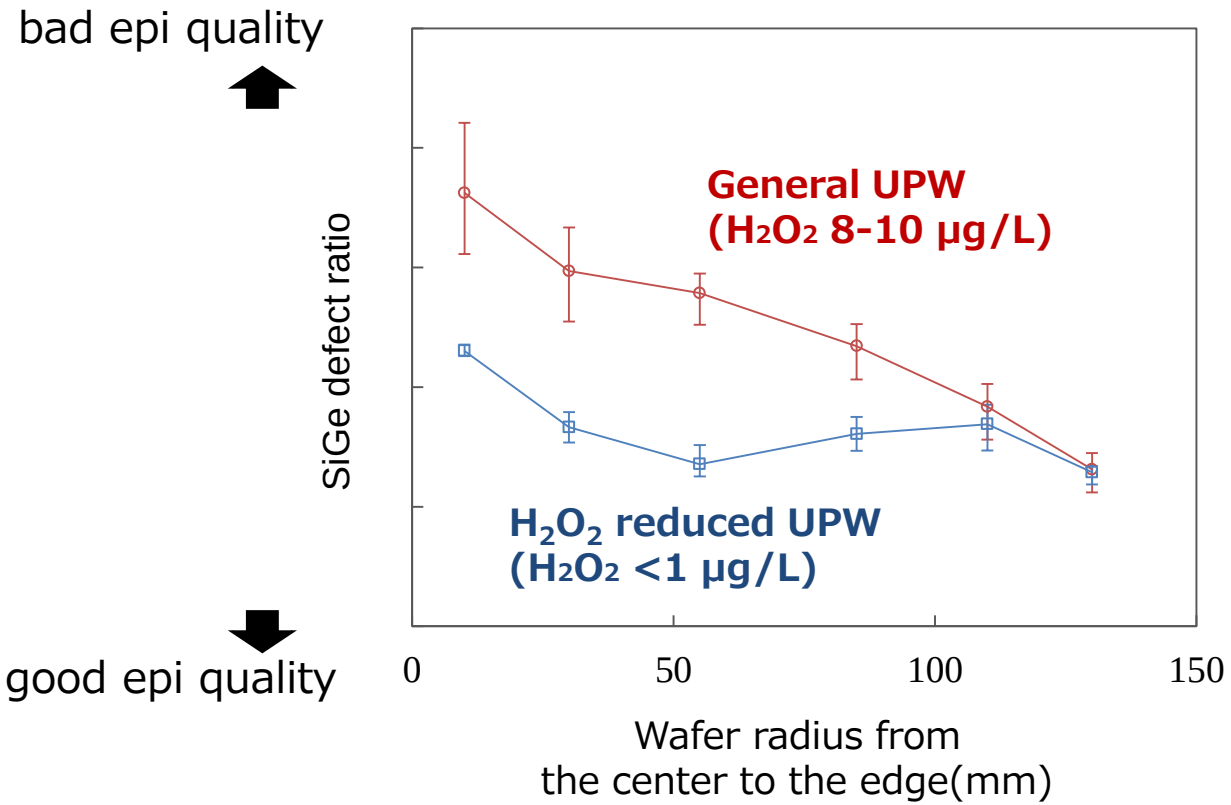

Fig. SiGe epi defect area on the wafer

SiGe epi quality can be improved by removing the dilute H_2O_2 in the UPW.

What has happened on the Si(100) surface by such a dilute H_2O_2?

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Why has Si(111) been chosen?

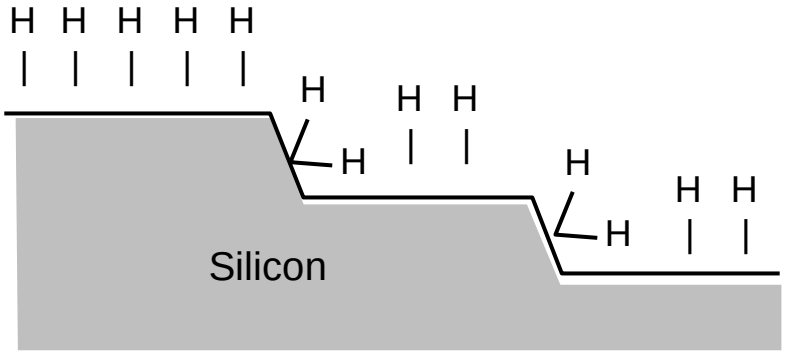

Fig. Surface image of Si(111)

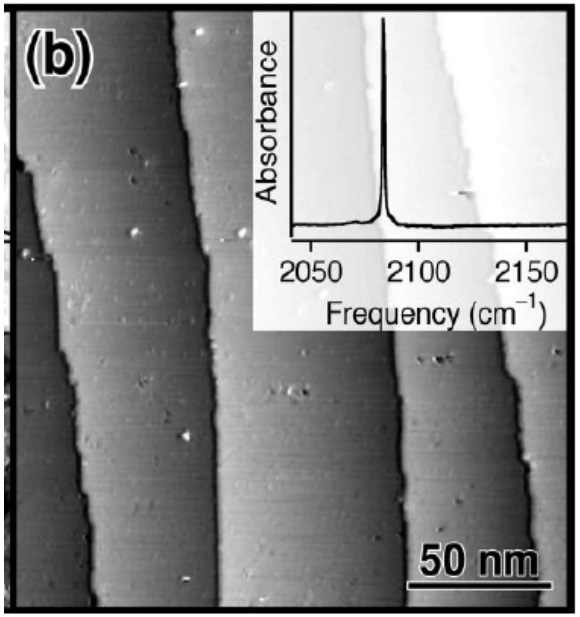

Fig. AFM image and FT-IR-ATR peak of Si(111)
[M.A. Hines, *Annu Rev Phys Chem.,* 54, 29-56 (2003)]

Si(111) surface: Terrace width with atomic steps, dominated by Mono-hydrogen termination

Si(111) will help to understand the impact of the dilute H_2O_2 on Si(100) due to its sensitivity for the state variation.

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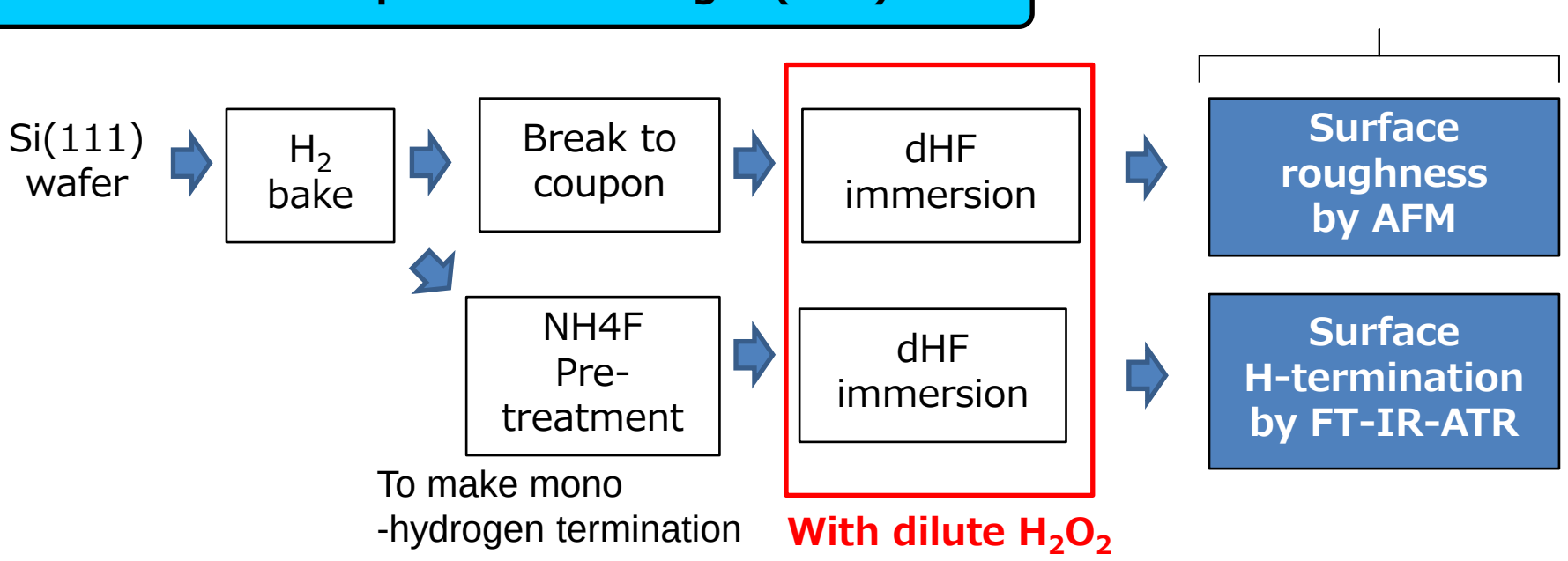
Process flow of experiments using Si(111)



Contents	Test Conditions
Surface roughness measurement **by AFM**	**H_2O_2 100 µg/L** in 0.7%HF, N_2 bubbling, Immersion: 15, 30min
Surface H-termination measurement **by FT-IR-ATR**	**H_2O_2 <1, 30, 100 µg/L** in 0.5%HF, DO: 60ppb Immersion: 15min

AFM and FT-IR-ATR were used to clarify the impact of the dilute H_2O_2 in dHF on Si(111) surface.

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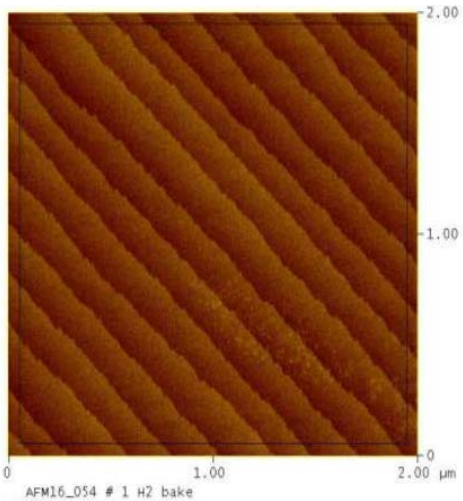
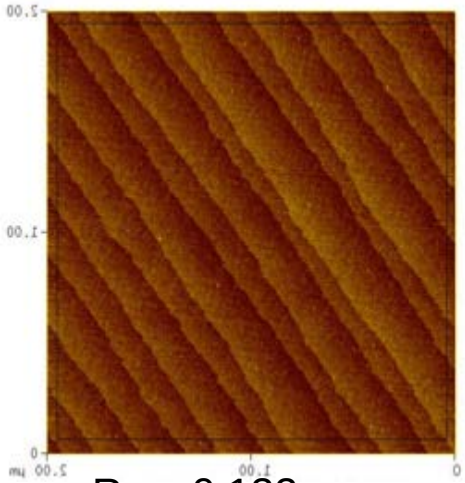
Result: AFM image on Si(111)

After H_2 bake



Rms 0.120nm
Ra 0.097nm

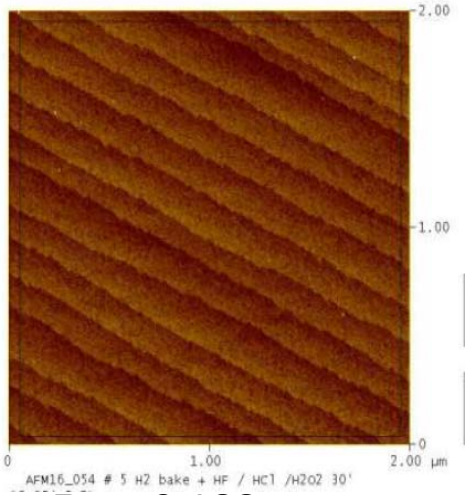
15min immersion



Rms 0.132nm
Ra 0.106nm

dHF with
100 µg/L H_2O_2

30min immersion



Rms 0.122nm
Ra 0.099nm

No clear difference between before and after immersion in dHF with 100 µg/L H_2O_2 was observed.

Si surface is not roughened by such a dilute H_2O_2.

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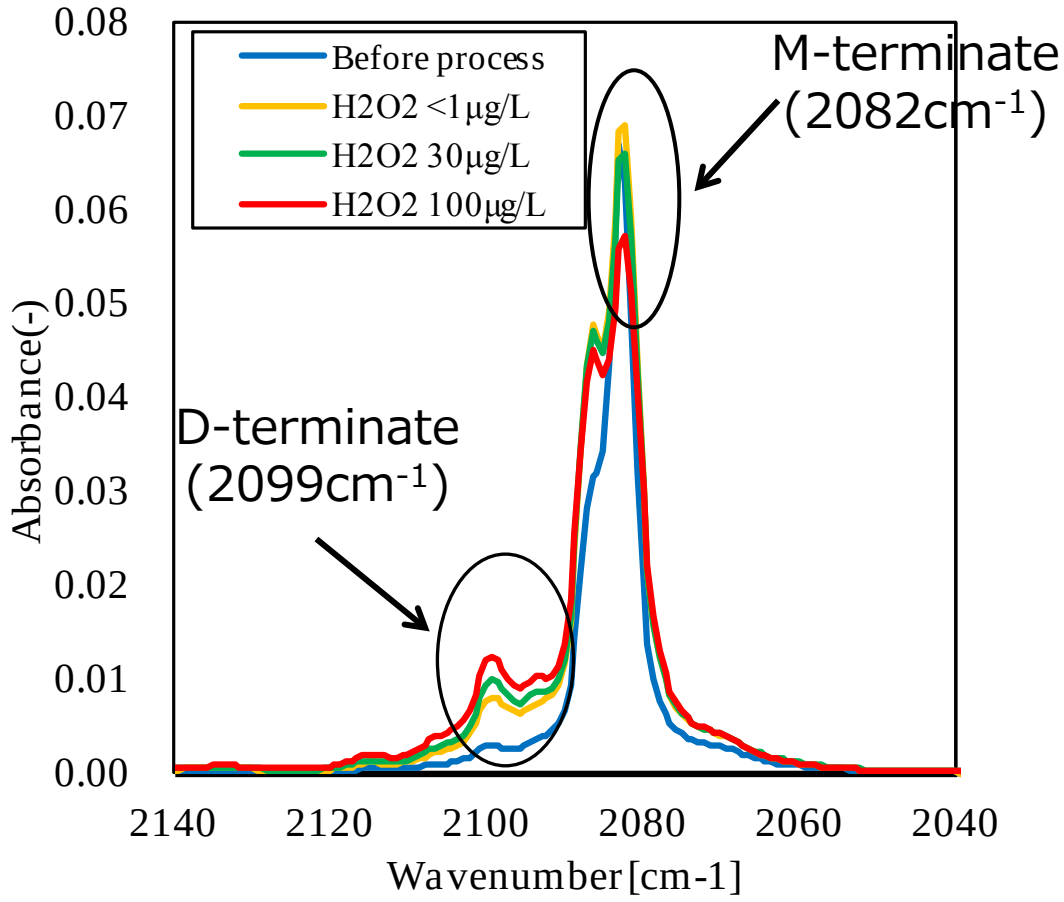
Result: FT-IR-ATR peak on Si(111)



M-terminate is decreased while D-terminate is increased when the dilute H_2O_2 exists in the dHF .

Dilute H_2O_2 promotes Si oxidation, and the oxide is etched by dHF.
So, the hydrogen–termination status has changed.

Possible mechanism of the dilute H_2O_2 impact on Silicon

1. During dHF process, the dilute H_2O_2 promotes oxidizing the surface of Si(111).and the oxide is etched by dHF. By the oxidation and etching, the hydrogen termination status on Si(111) has changed.

2. Same reaction would happen on Si(100) by the dilute H_2O_2. These is a possibility that the same mechanism of the dilute H_2O_2 impact may happen on Si(100) also.

3. H_2O_2 may be one of the main factors of the SiGe epi defects.

Still work will be needed to support the above-mentioned possible mechanism

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Summary

The SiGe epitaxial quality has been improved by H_2O_2 removed UPW compared with the dilute H_2O_2 containing UPW.

FT-IR-ATR measurements indicate an impact of the dilute H_2O_2 on the Si (111) surface morphology. Silicon can be etched by dHF solution involving dH_2O_2.

So it is assumed that H_2O_2 is one of the main factors which make the SiGe epi quality low.

H_2O_2 in UPW affects the production of semiconductors.

→Kurita Pt catalyst will solve this problem.

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We can support quality stabilization of semiconductor products.

Not just water, Creativity

Thank you for your attention

KURITA WATER INDUSTRIES LTD.