Interfacial Nano Electrochemistry
Adsorption WG activity summary

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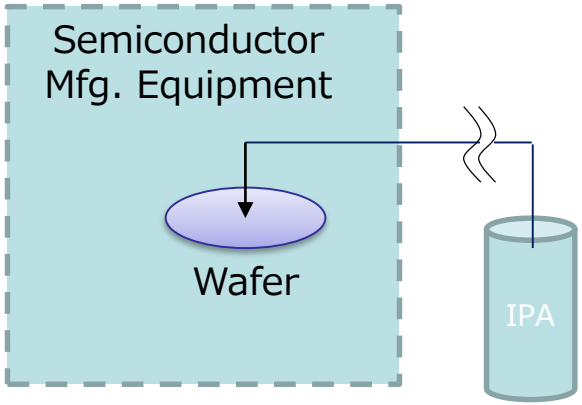
Background

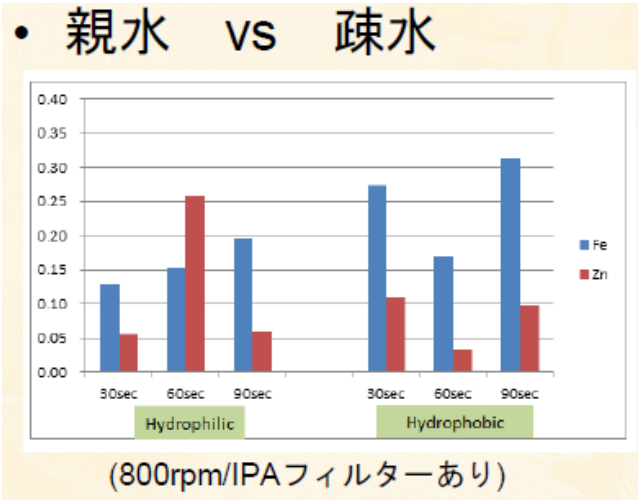
- Standardization of cleanliness evaluation method for semiconductor manufacturing equipment was studied in 2014 by SEMI UPL-SG(Ultrapure Liquid Evaluation Study Group).

- It was considered to analyze the liquid medium passing through the equipment to confirm the cleanliness. Correlation between wafer contamination and the liquid quality was needed to be confirmed.
- Due to the dispense of liquid IPA (2-propanol) for drying the wafer with preventing the pattern collapse as semiconductor structure is miniaturizing and A/R becomes higher, influence of metal impurity in IPA as test medium is studied.

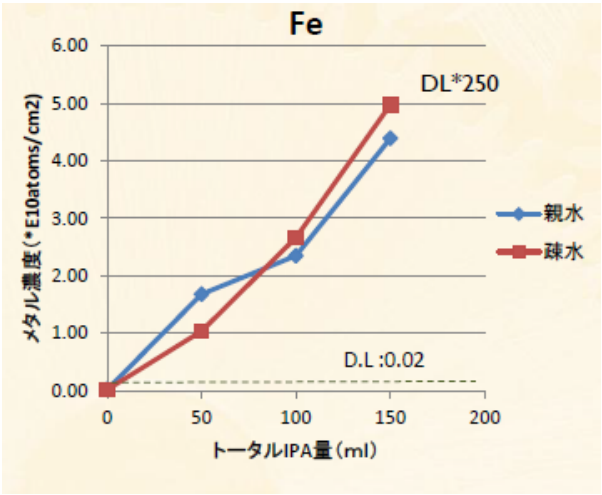
Background



- IPA was dispensed on the wafer and metal density on the wafer was measured.
- Test was conducted with varying the dispense condition (time, spin speed, volume, etc.), type of wafers (hydrophilic, hydrophobic) and/or filters (with, without).
  * at SCREEN and/or at TEL



* SCREEN's data in SEMI report

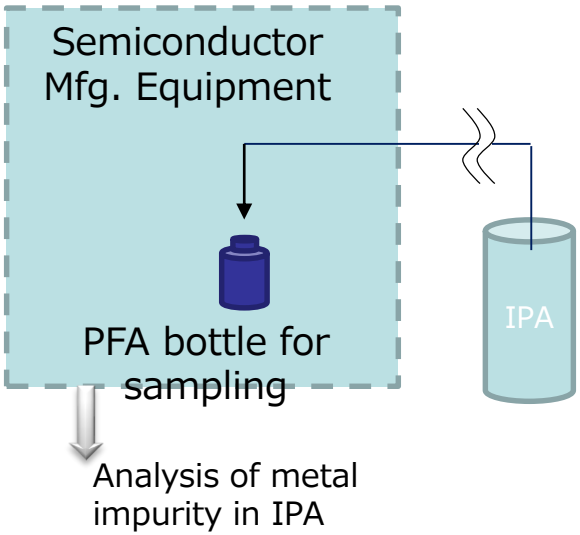


* TEL's data in SEMI report

Fe density on the wafer increased as IPA dispense volume increases.

Background

- Analysis of metal impurity in IPA dispensed onto wafer.



Item	Unit	2-Propanol (Taken from the nozzle)
Ag	ppt	1 or below
Al	ppt	1
Ba	ppt	1 or below
Bi	ppt	1 or below
Ca	ppt	1 or below
Cd	ppt	1 or below
Co	ppt	1 or below
Cr	ppt	2
Cu	ppt	1
Fe	ppt	7
Ga	ppt	1 or below
K	ppt	1
Li	ppt	1 or below
Mg	ppt	1 or below
Mn	ppt	1 or below
Na	ppt	4
Ni	ppt	1
Pb	ppt	1 or below
Sr	ppt	1 or below
Zn	ppt	1 or below

The sample was analyzed by Toshiba Nanoanalysis (TNA) and KANTO CHEMICAL and both show Fe density below or equal to 10ppt.

Background

分析値 unit:*E10 atoms/cm2

	表面状態	IPA	液量(ml)	Li	Na	Mg	Al	K	Ca	Ti	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ge	Sr	Mo	Ba	W
Receipe A	親水	30	50	-	0.08	-	0.03	0.05	-	-	-	-	1.7	-	-	-	-	0.17	-	-	-	-
Receipe A	親水	60	100	-	0.04	-	0.04	-	-	-	-	-	2.3	-	0.01	0.02	-	0.21	-	-	-	-
Receipe A	親水	90	150	-	0.04	-	0.05	-	-	-	0.01	-	4.4	-	0.02	0.02	-	0.24	-	-	-	0.01
Receipe A	疎水	30	50	-	0.13	-	0.07	-	-	-	-	-	1.0	-	-	0.05	-	0.07	-	-	-	-
Receipe A	疎水	60	100	-	0.08	-	0.08	-	-	-	0.01	-	2.7	-	0.02	0.06	-	-	-	-	-	-
Receipe A	疎水	90	150	-	0.11	-	0.09	-	-	-	0.02	-	5.0	-	0.02	0.07	-	-	-	-	-	-
Receipe B	親水	30	8.3	-	0.18	-	0.04	0.17	-	-	-	-	0.49	-	-	0.01	0.06	0.17	-	-	-	0.01
Receipe B	親水	60	8.3	-	-	-	0.04	-	-	-	-	-	0.68	-	-	0.02	-	0.17	-	-	-	0.01
Receipe B	親水	90	8.3	-	-	-	0.05	-	-	-	-	-	0.71	-	-	0.02	-	0.17	-	-	-	0.01
Receipe B	親水	300	8.3	-	-	-	0.07	-	-	0.04	0.01	-	0.71	-	-	0.04	-	0.17	-	-	-	0.01
Receipe B	疎水	30	8.3	-	0.02	0.03	0.04	-	-	-	-	-	0.55	-	-	0.04	-	0.06	-	-	-	-
Receipe B	疎水	60	8.3	-	0.03	-	0.05	-	-	-	0.01	-	0.72	-	-	0.04	-	-	-	-	-	-
Receipe B	疎水	90	8.3	-	0.04	-	0.06	-	-	-	0.01	-	0.77	-	-	0.04	-	-	-	-	-	-
Receipe B	疎水	300	8.3	-	0.04	-	0.08	-	-	0.05	0.02	-	0.95	-	0.01	0.05	-	0.06	-	-	-	-
Ref	親水	—	–	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.13	-	-	-	0.01
Ref	疎水	–	–	-	-	-	-	-	-	-	-	-	-	-	-	0.03	-	0.06	-	-	-	-
定量下限				0.02	0.02	0.02	0.02	0.02	0.05	0.03	0.01	0.01	0.02	0.01	0.01	0.01	0.04	0.06	0.01	0.01	0.01	0.01

※-は定量下限換算値以下

＊＊ TEL's test data in SEMI report

Dispense condition of 5×10^{10}atoms／cm^2, 150ml as volume, onto the 300mm wafer

【Fe total volume（weight) on 300mm wafer】
5E^{10}（atoms/cm^2）x π15^2（cm^2）/6.02E^{23}（atoms/mol）x 55.85（g/mol　Fe atomic weight）×E^9（ng／g）　＝ **3.28（ng）**

Background

- Under the assumption that 100% of Fe atoms in the liquid adsorb to the wafer,
  3.28(ng/0.15L)×0.7863(kg/L) ≒ 17(ng/kg)
  equivalent to 17ppt (22ng/L)
- Under the assumption of 50% (half of IPA atoms in IPA) adsorption, 34ppt
- These figures are inconsistent with liquid analysis of 10ppt or below. (adsorption ratio over 100%)
- Wafer analysis's by SCREEN and TEL show similar result even those conducted by two different method (TXRF, ICP-MS).

Therefore, as “an analysis of the mechanism for impurities in IPA being adsorbed onto the wafer, some questions came out as follows:

1. Is Fe collectivity low during chemical analysis?
2. Why adsorption ratio onto the wafer is high?

INE decided to investigate these question deeply in the Working Group.

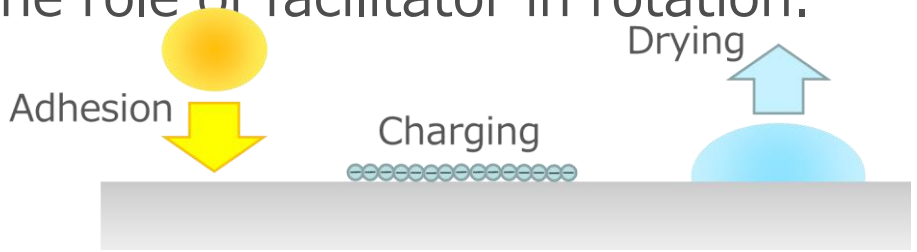
Adsorption WG activity

- Phenomena and verification result were discussed in three small Working Groups (WG) in INE.
- In the Adsorption WG, lectures were given mainly in the first half and discussion was held in among participants in the second half.
- Mr. Yoshimizu from Toshiba lead the WG and each of participants took the role of facilitator in rotation.

・Adsorption WG (Material adsorption onto the interface)

・Charging WG（Interfacial Charging）

・Drying WG（Liquid discharge from interface）



Cross field industrial and academic activity

* Mr. Kosai, TEL

2nd Poster Presentation

WG office

・Y. Yoshimizu, Toshiba

・H. Araki, SCREEN SPE

・Y. Yoshida, KANTO CHEMICAL

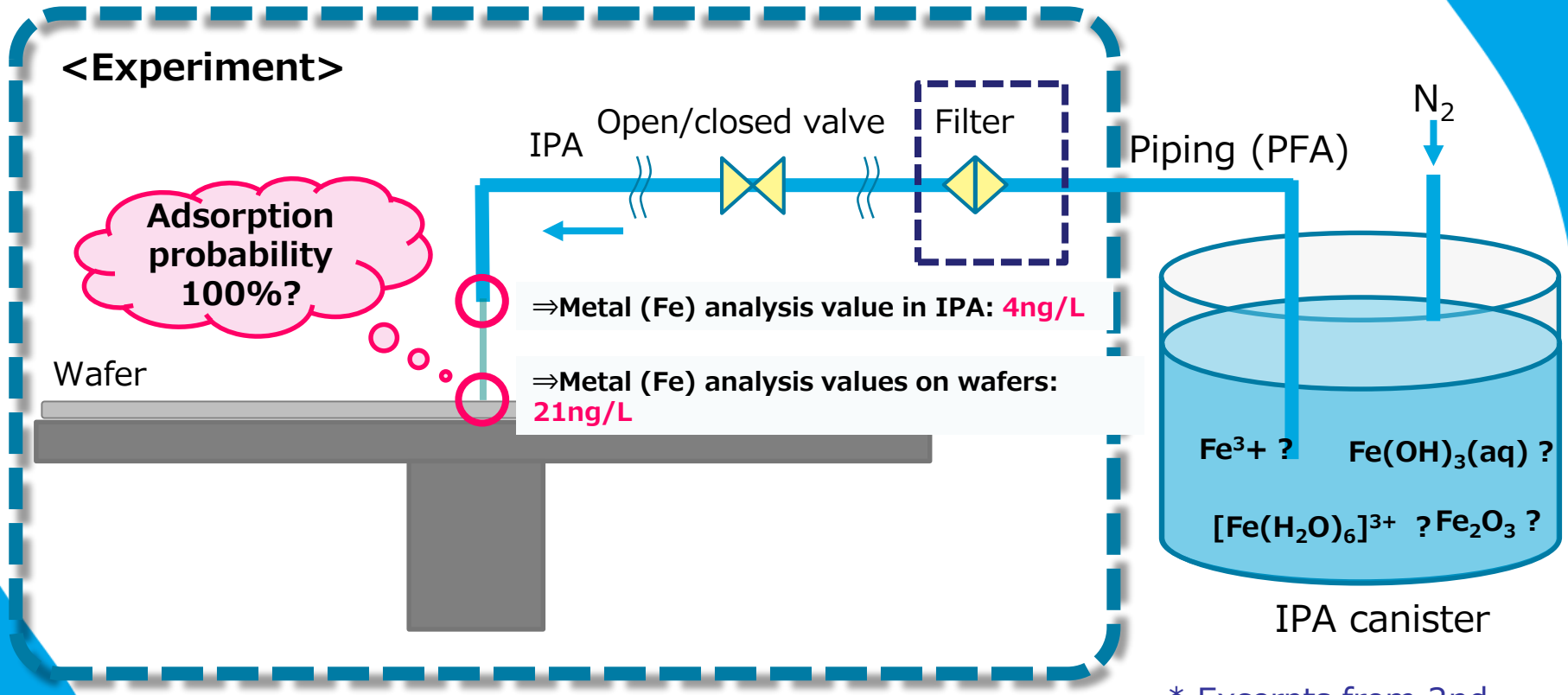
Adsorption WG Activity

	Date	Venue	Facilitator	Remark/ Lecture
Kick off	2015.02.05	SEMI Japan	—	Preparation for WG
1st WG	2015.05.24	Kyoto University	I. Kondo (RION)	Eiichi Yamaguchi (Kyoto University) "Elucidation of science innovation phenomenon and resonance field of tacit knowledge" Yoshihiro Mori (Horiba)"Adsorption of metallic impurities in chemical solution on Si wafer surface"
2nd WG	2015.06.18	Kanto Chemical	H. Sugawara (Organo)	Yasuo Kameda (Yamagata University) "Metal form in nonaqueous solvent"
3rd WG	2015.08.28	Tokyo Electron	M. Saito (Tokyo Electron)	Katsuhiko Kawabata (Ias) "Pretreatment method for metal analysis in IPA" Katsuo Mizoguchi (Agilent) "ICPMS analysis technique for metal analysis in IPA"
4th WG	2015.11.27	SCREEN	H. Araki (SCREEN)	Katsunemi Izumi (Izumi Patent Office) "Visualization of tacit knowledge" Intermediate Review
5th WG	2016.02.03	SCREEN	T. Nagabuchi (Entegris Japan)	Kenta Arima (Osaka University) "Extreme level surface creation process and cleanup technology"
	2016.03.18	Keio University	K. Kosai (Tokyo Electron)	Activity report at the 2nd INE poster presentation exhibition
6th WG	2016.05.12	SCREEN	M. Sato (SCREEN)	Ryo Shirakashi (Tokyo University) "Quantitative measurement of bound water and free water and its application")
6.5th WG	2016.06.30	SCREEN	D. Yano (Organo)	Discussion continued from 6th WG.
7th WG	2016.09.27	SCREEN	T. Takakura (Nihon Pall)	Motoyoshi Kobayashi (Tsukuba University) "Consider the aggregate dispersion of colloids from the zeta potential"

Summary reported at 3rd Poster Presentation Exhibition (2018.03.19)

Report 1: Form of Fe in IPA

- Kick off ~ 1st WG



Motivation to unravel the mechanism!
(Adsorption WG established)

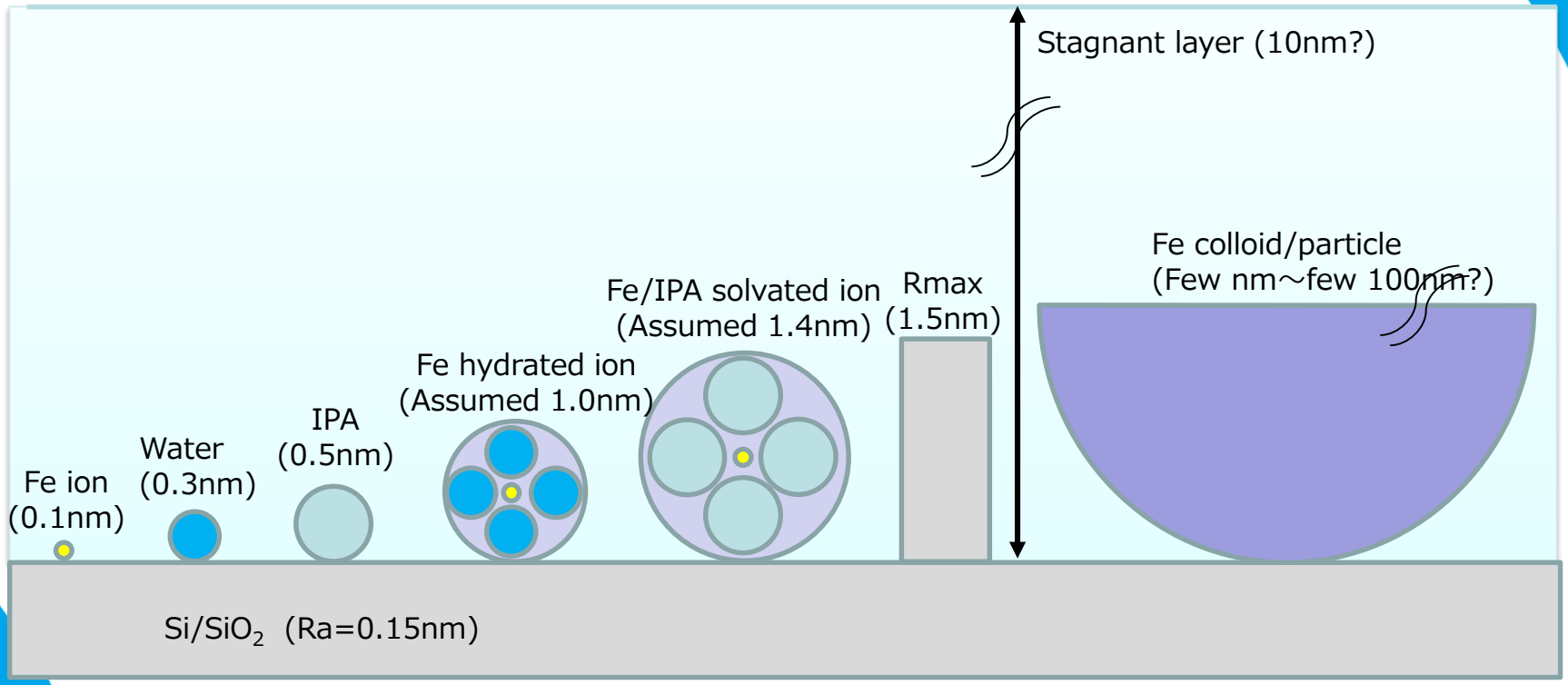
1st WG

* Excerpts from 2nd Poster Exhibition
Mr. Kosai, TEL

Report 1: Form of Fe in IPA

- 2nd WG

Fe adsorption to Si wafer surface in IPA (image)



* An excerpt from the material of Mr. Sugawara (Organo) and Mr. Kosai (TEL)

Report 1: Form of Fe in IPA

Result of X-ray diffraction, quantum mechanics, and molecular dynamics simulation for Fe form in IPA

☆ Data provision: Professor Yasuo Kameda, Faculty of Science, Yamagata University

X-ray diffraction experiment

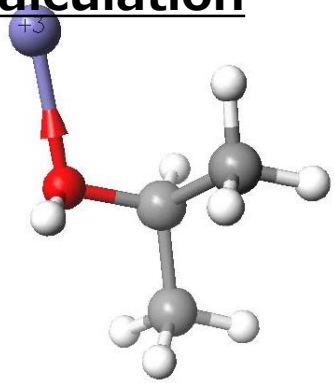
Fe-O distance (r) and coordination number (n) in solution

・r in aqueous solution ($Fe^{3+}\cdots O$) = 0.201nm, n=6

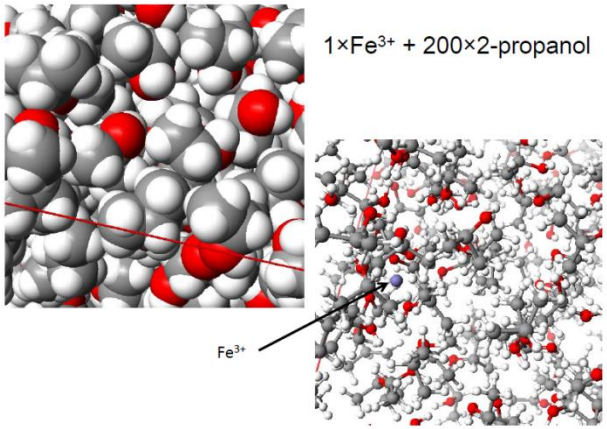
・r in IPA solution ($Fe^{3+}\cdots O$) = 0.212nm, n=6

→Fe3 + ・・・O interaction in IPA solution is slightly weaker than that in aqueous solution.

Quantum mechanics calculation



Molecular dynamics Simulation



* Excerpts from 2nd Poster Exhibition Mr. Kosai, TEL

Report 1: Form of Fe in IPA

Impurity quantity in IPA (molecule, ion, particle /L)

IPA 8×10^{24} /L

Impurity
- Water (<0.01%) (include H^+OH^- ion) ≦ 3×10^{21} /L
- Metal (Fe<10ppt) ≦ 1×10^{14} /L
- Particle (≧200nm) ≦ 1×10^{5} /L

→Majority of impurities in IPA are water (H2O). Water (H2O) as an impurity may be coordinated around Fe.

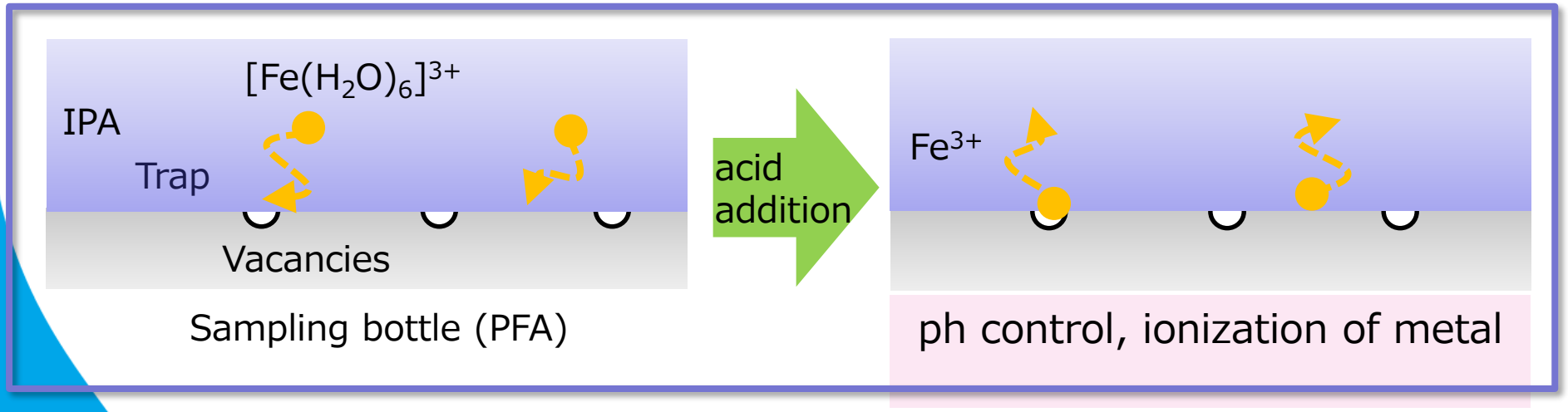
In IPA, Fe is likely to be present by forming a hydrate $[Fe(H_2O)_6]^{3+}$ (Presumed)

* An excerpt from the material of Mr. Sugawara (Organo) and Mr. Kosai (TEL)

Report 2: Fe analysis in IPA

- 3rd WG

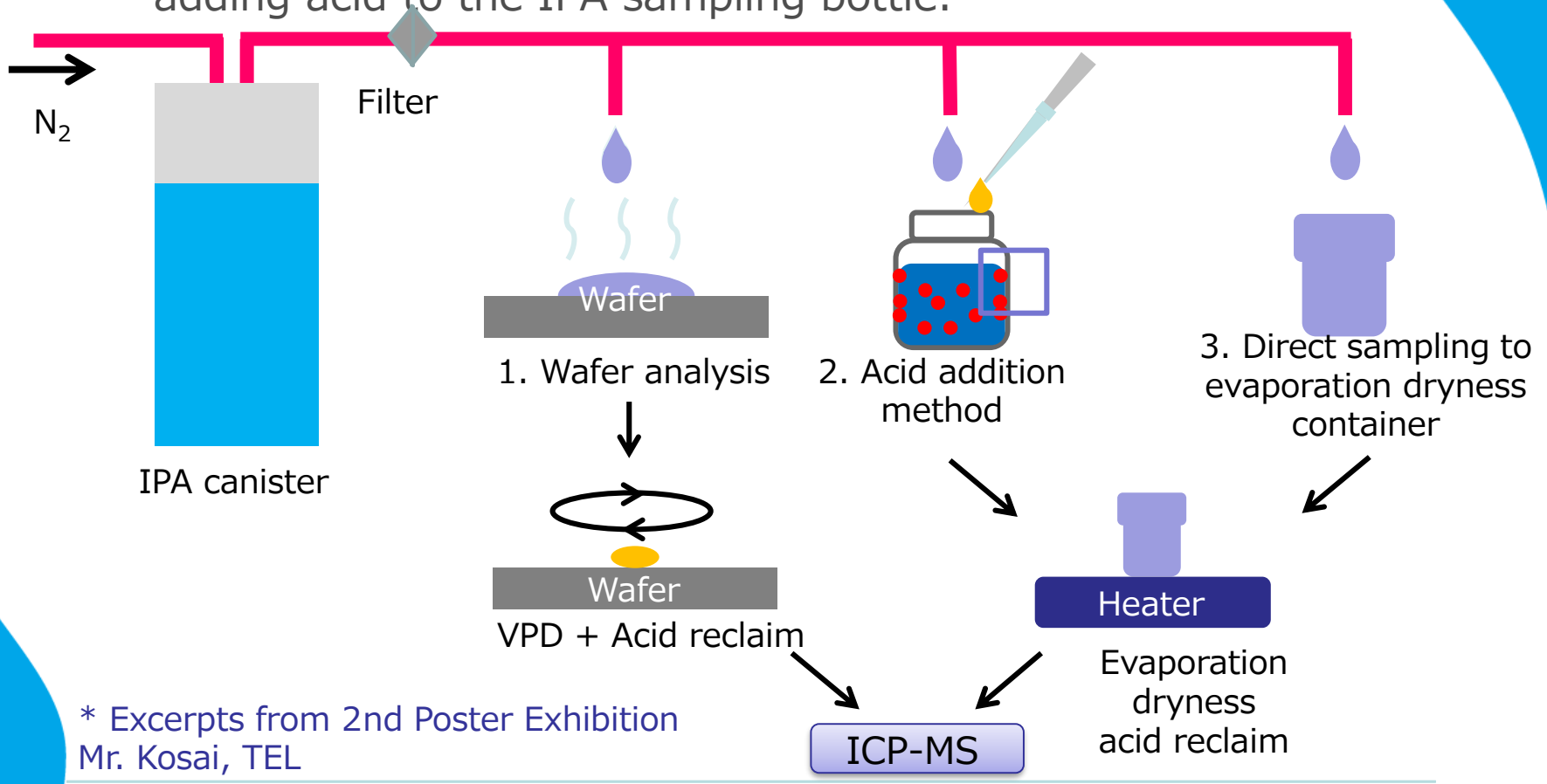
  Consideration of "adsorption" phenomenon onto the container wall (PFA) as a factor of low recovery in ICP-MS measurement in Fe analysis in IPA



* Excerpts from 2nd Poster Exhibition
Mr. Kosai, TEL

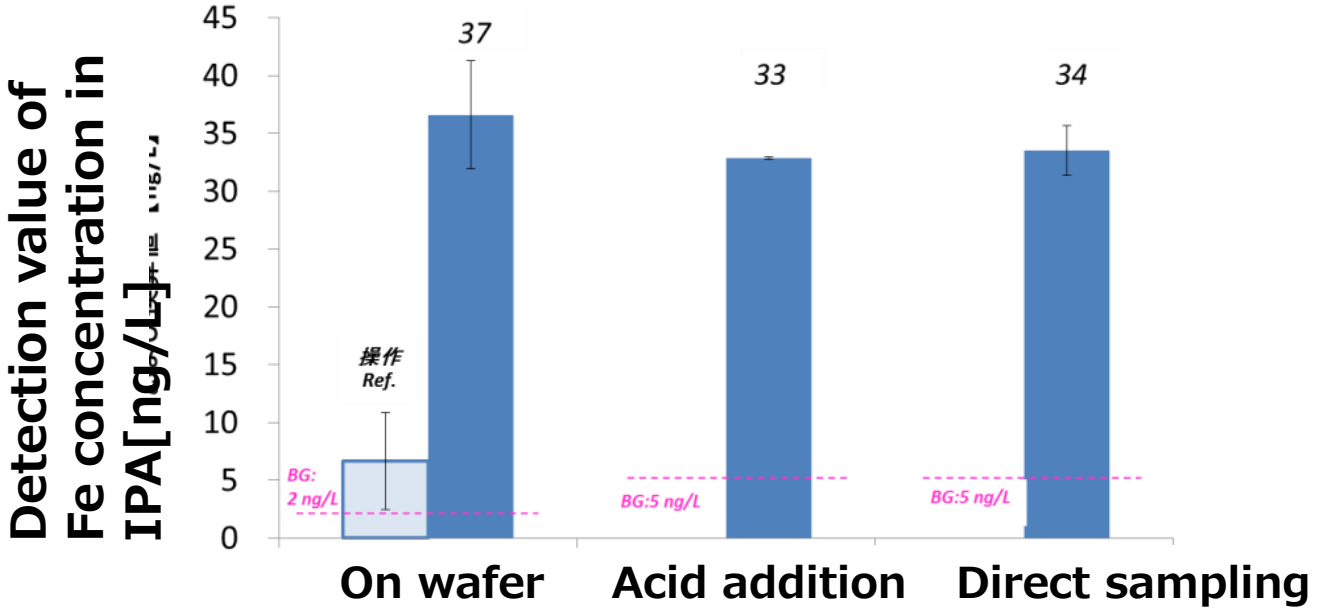
Report 2: Fe analysis in IPA

- 4th WG Conducted a verification experiment by adding acid to the IPA sampling bottle.



* Excerpts from 2nd Poster Exhibition
Mr. Kosai, TEL

Report 2: Fe analysis in IPA



Correlation between on-wafer analysis and analysis by acid addition and direct sampling was obtained.
Results supporting the adsorption model to the sampling bottle

The reason that the adsorption probability onto the wafer exceeds 100% is presumed because FE has adsorbed to PFA container

* Excerpts from 2nd Poster Exhibition, Mr. Kosai,TEL

Report 3: Adsorption behavior of metallic impurities in IPA onto wafers

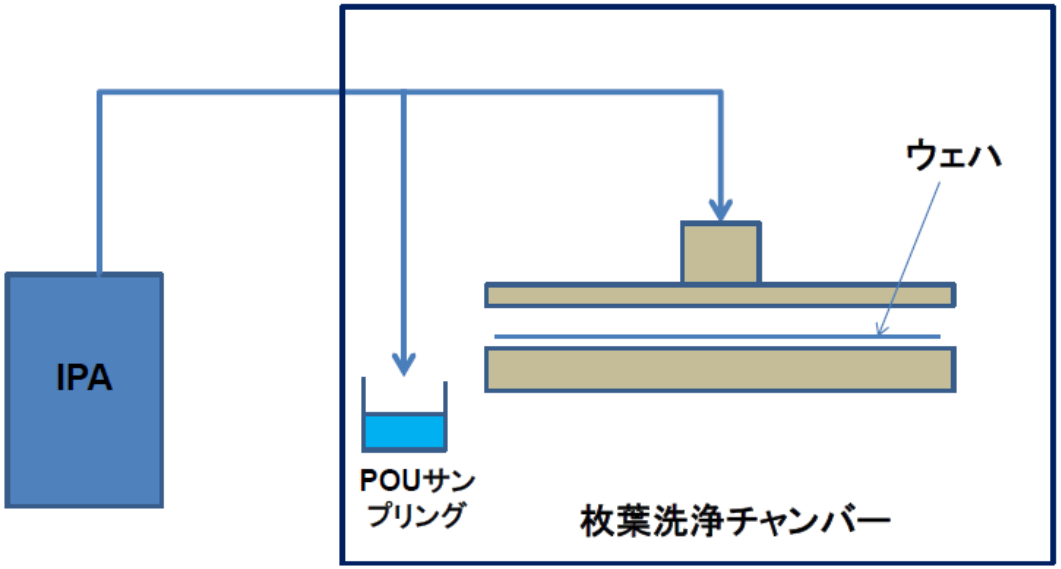
- 5^{th} WG ~ 7^{th} WG

The phenomenon that Fe value in IPA is low is presumed to be an adsorption phenomenon to the sample container inner wall for analysis. It seems rather high that the liquid of about 30 ~ 50ppt flows on the wafer and about half of that remains on the wafer.

To think about adsorption to Si wafer surface, we conducted a verification experiment at SCREEN and at IAS.

Report 3: Adsorption behavior of metallic impurities in IPA onto wafers

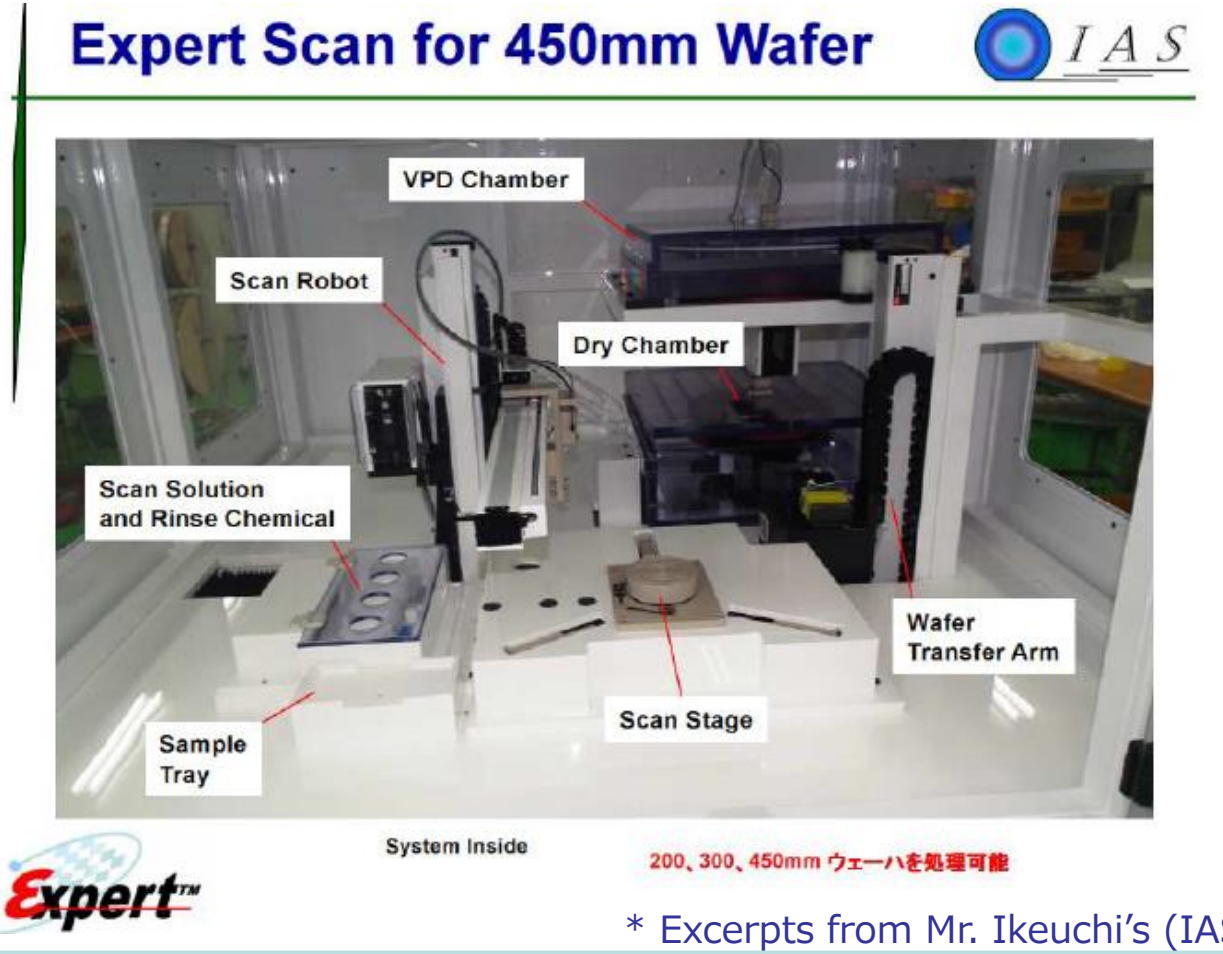
- In the experimental system using equipment at SCREEN, correlation between various parameters below and adsorption amount was confirmed.
- (1) IPA flow rate (2) wafer rotational speed (3) Process time (4) hydrophobic or hydrophilic wafer surface (5) Presence of UPW pre-wet before applying IPA (6) Fe concentration in IPA



* Excerpts from Mr. Sato's (SCREEN) material

Report 3: Adsorption behavior of metallic impurities in IPA onto wafers

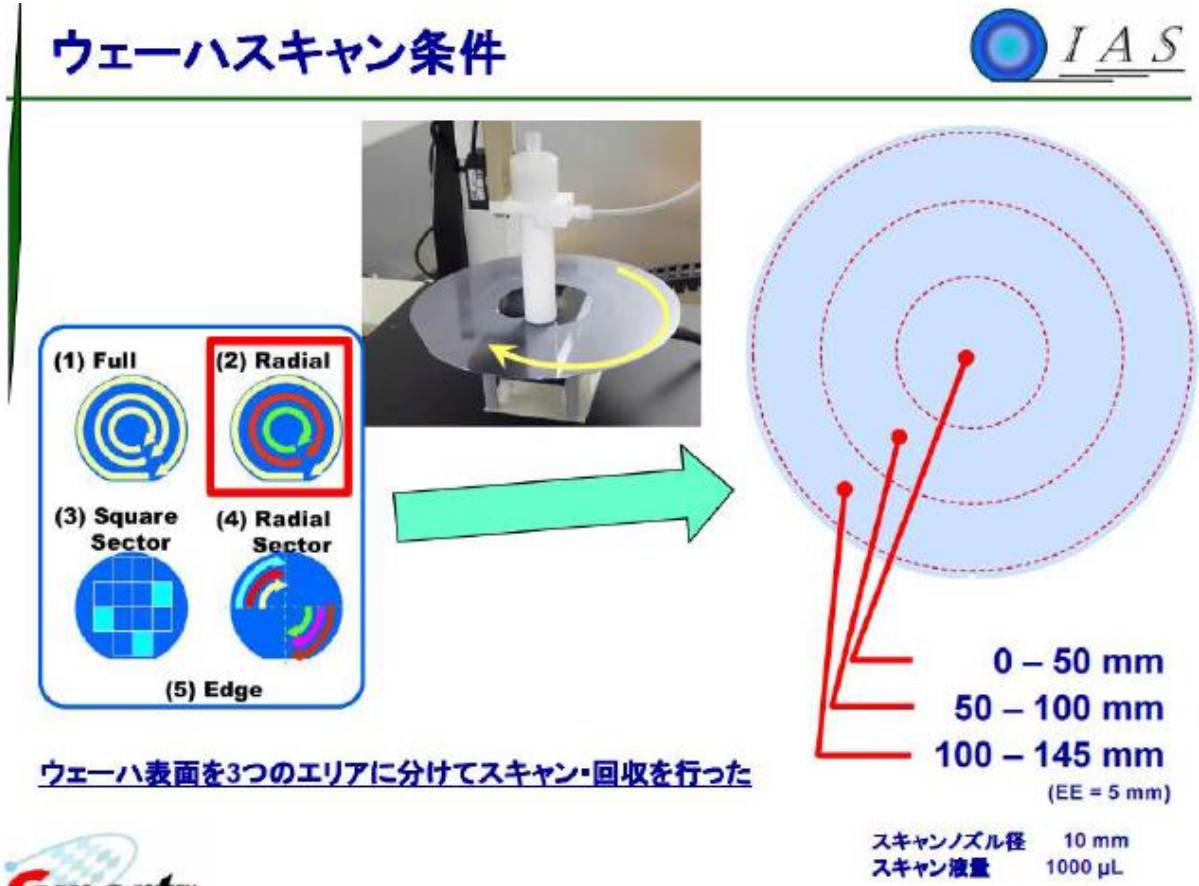
- Sampling equipment for wafer surface metal analysis



* Excerpts from Mr. Ikeuchi's (IAS) material

Report 3: Adsorption behavior of metallic impurities in IPA onto wafers

- Sampling equipment for wafer surface metal analysis



* Excerpts from Mr. Ikeuchi's (IAS) material

Report 3: Adsorption behavior of metallic impurities in IPA onto wafers

- Results of Fe analysis of wafer surface in each condition

処理順序	SlotNo.	ウエハ		IPA			Fe E10 atm/cm2			ウエハ上 Fe [atm]				元のIPA濃度補正後(ppb)	補正後IPA中鉄個数(atm/L)	供給 Fe量 [atm	付着率 [%]
		表面	直前	流量	回転数	時間	0-50mm	50-100mm	100-145mm	0-50mm	50-100mm	100-145mm	Total				
2	2	疎水	Dry	100	300	10	0.591	0.3	0.219	4.64E+11	7.07E+11	7.59E+11	1.93E+12	0.094	1.01E+15	1.69E+13	11.43
3	3	親水	Dry	100	300	10	0.305	0.118	0.091	2.4E+11	2.78E+11	3.15E+11	8.33E+11	0.0885	9.54E+14	1.59E+13	5.24
14	4	親水	Dry	200	300	10	0.163	0.061	0.068	1.28E+11	1.44E+11	2.36E+11	5.07E+11	0.028	3.02E+14	1.01E+13	5.04
15	5	親水	Dry	300	300	10	0.132	0.057	0.068	1.04E+11	1.34E+11	2.36E+11	4.74E+11	0.0225	2.43E+14	1.21E+13	3.90
4	6	親水	Dry	100	500	10	0.289	0.133	0.13	2.27E+11	3.13E+11	4.5E+11	9.91E+11	0.083	8.95E+14	1.49E+13	6.64
5	7	親水	Dry	100	800	10	0.306	0.189	0.132	2.4E+11	4.45E+11	4.57E+11	1.14E+12	0.0775	8.35E+14	1.39E+13	8.21
6	8	親水	Dry	100	300	30	0.111	0.115	0.089	8.72E+10	2.71E+11	3.08E+11	6.66E+11	0.072	7.76E+14	3.88E+13	1.72
7	9	親水	Dry	100	300	60	0.895	0.289	0.137	7.03E+11	6.81E+11	4.75E+11	1.86E+12	0.0665	7.17E+14	7.17E+13	2.59
8	10	疎水	DIW	100	300	10	0.124	0.082	0.079	9.74E+10	1.93E+11	2.74E+11	5.64E+11	0.061	6.58E+14	1.10E+13	5.15
9	11	親水	DIW	100	300	10	0.057	0.078	0.077	4.48E+10	1.84E+11	2.67E+11	4.95E+11	0.0555	5.98E+14	9.97E+12	4.97
16	12	親水	DIW	300	300	10	0.011	0.025	0.053	8.64E+09	5.89E+10	1.84E+11	2.51E+11	0.017	1.83E+14	9.16E+12	2.74
10	13	親水	DIW	100	800	10	0.117	0.086	0.213	9.19E+10	2.03E+11	7.38E+11	1.03E+12	0.05	5.39E+14	8.98E+12	11.49
11	14	親水	DIW	100	300	60	0	0.056	0.054	0	1.32E+11	1.87E+11	3.19E+11	0.0445	4.80E+14	4.80E+13	0.66
12	15	親水	DIW	-	-	-	N.D.	N.D.	N.D.	0	0	0	0	0.039	4.20E+14	N/A	N/A
13	16	親水	Dry	100	10	10	4.059	0.379	0.563	3.19E+12	8.93E+11	1.95E+12	6.03E+12	0.0335	3.61E+14	6.02E+12	100.20

■The amount of Fe per wafer is calculated from the results of surface analysis from each area on the wafer.

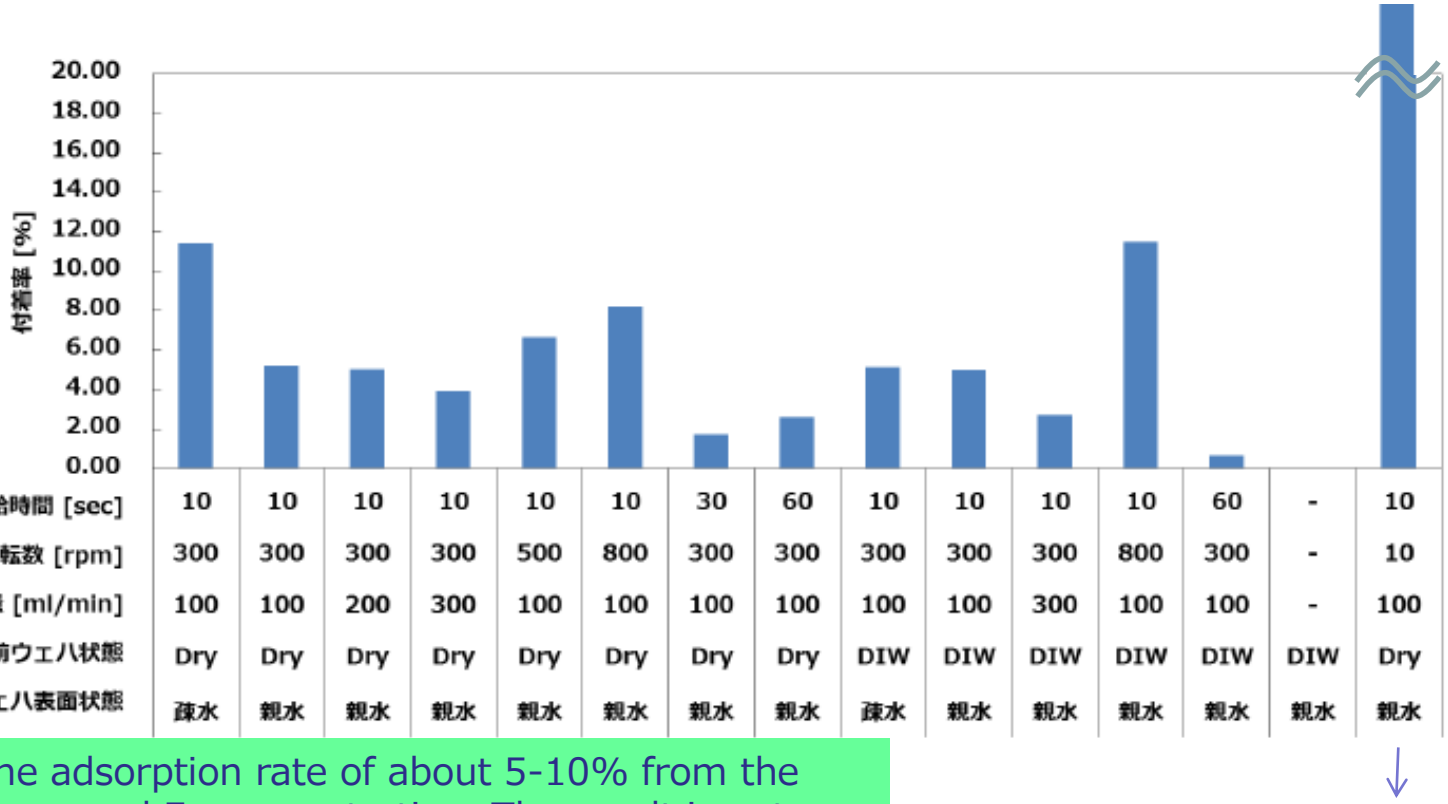
↓

■Adsorption rate calculated from here

* Excerpts from Mr. Sato's (SCREEN) material

Report 3: Adsorption behavior of metallic impurities in IPA onto wafers

- Results of Fe analysis of wafer surface in each condition



IPA供給時間 [sec]	10	10	10	10	10	10	30	60	10	10	10	10	60	-	10
IPA供給時回転数 [rpm]	300	300	300	300	500	800	300	300	300	300	300	800	300	-	10
IPA流量 [ml/min]	100	100	200	300	100	100	100	100	100	100	300	100	100	-	100
IPA供給前ウェハ状態	Dry	Dry	Dry	Dry	Dry	Dry	Dry	Dry	DIW	DIW	DIW	DIW	DIW	DIW	Dry
ウェハ表面状態	疎水	親水	親水	親水	親水	親水	親水	親水	疎水	親水	親水	親水	親水	親水	親水

The adsorption rate of about 5-10% from the presumed Fe concentration. The result is not more than 100% and considered as valid.

Condition of drying IPA on the wafer

* Excerpts from Mr. Sato's (SCREEN) material

Report 3: Adsorption behavior of metallic impurities in IPA onto wafers

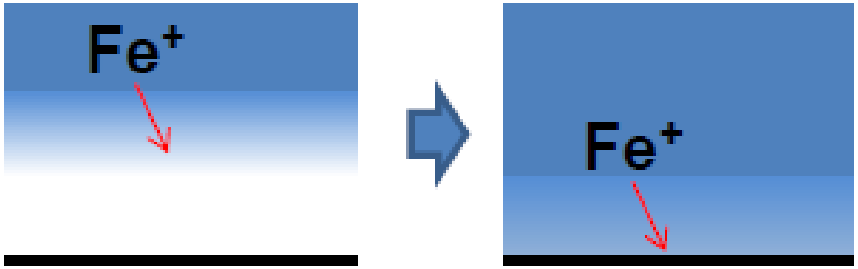
- As a result of the wafer surface FE analysis of each condition, the adsorption rate is analyzed.
- (1) Higher IPA flow rate (dispense amount per time)
- (2) Higher wafer rpm (fast rotation speed)
- (3) The surface of the wafer is hydrophobic
- (4) No UPW pre-wet before applying IPA

The tendency that the adsorption rate increases with these four condition is seen.

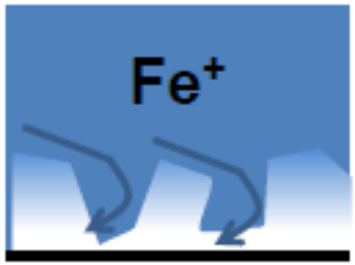
In each case above, it is considered the boundary layer of the fluid on the outermost surface of the wafer is thinner.

Report 3: Adsorption behavior of metallic impurities in IPA onto wafers

- The hypothesis was discussed that the Boundary Layer thinner, more the adsorption of Fe occurs.
-



When the Boundary Layer is thin, does probability of contacting Fe in the bulk of the fluid layer to the wafer increases?

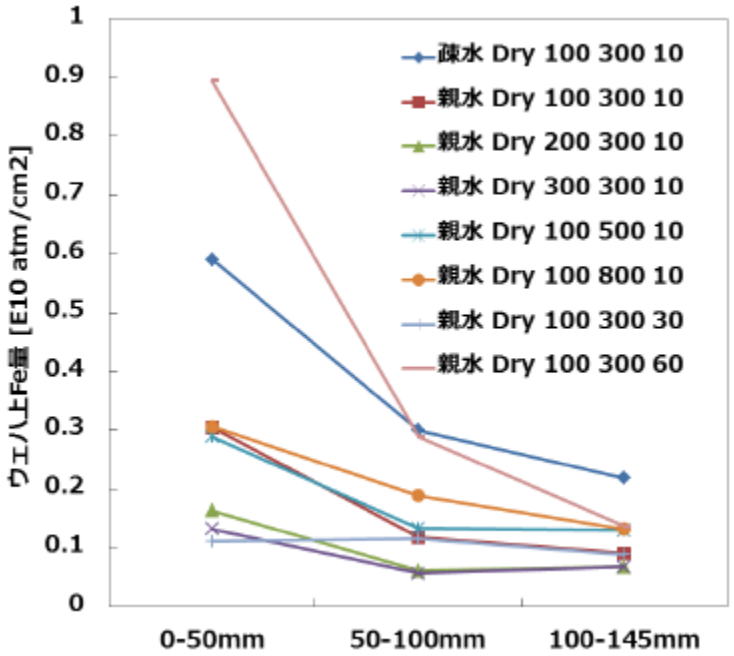


When the Boundary Layer collapses by turbulence, does probability of contacting Fe to the wafer increase?

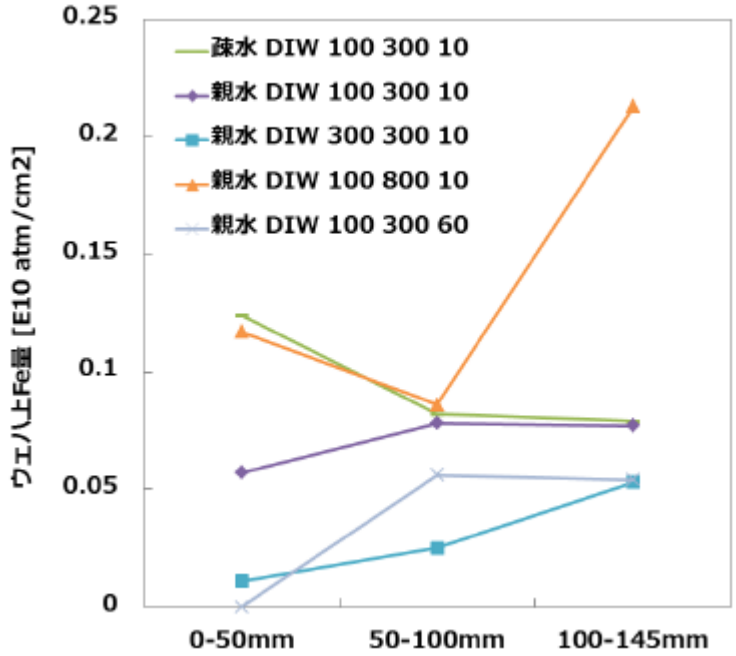
* Excerpts from Mr. Sato's (SCREEN) material

Report 3: Adsorption behavior of metallic impurities in IPA onto wafers

- Tendency of adsorption behavior from the center of the wafer to the edge.



IPA applied directly to the wafer



IPA applied after UPW pre-wet

Does no-prewetted-wafer have more Fe adsorption at the center part and does prewetted-wafer has more Fe at the edge part?

* Excerpts from Mr. Sato's (SCREEN) material

Report 3: Adsorption behavior of metallic impurities in IPA onto wafers

- The adsorption rate at the center area of the wafer is high by directly dispensing IPA.

  ↓

- Center area is considered that boundary layer is thin by the droplet or high angular velocity by wafer rotation or the possibility of turbulent generation is high.

  ↓

- Is the hypothesis correct…?

Although even 5 ~ 10% seems rather high considering the ratio of Boundary layer in the bulk layer and adsorption ratio, many tendencies are confirmed by the experiment with various conditions.

Summary

- The cause for more Fe amount detected from the wafer than Fe in IPA was because the reclaim rate decrease to ICP-MS occurred due to the Fe adsorption to inner wall of sampling container.
- As the Fe adsorption behavior to the Si wafer, it was assumed thought the experiment with various conditions that the turbulent occurred between the laminar flows and/or thickness of boundary layer are related.

【Issues to be clarified】

- Transport model of Fe in IPA based on calculation or measurement of fluid behavior on wafers
- Quantification of Fe adsorption behavior to solid surface

Thanks

- I thank Mr. Yoshimizu (Toshiba Memory) who managed each WG as a leader of the adsorption WG and Mr. Araki (SCREEN) who run WG together.
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Thank you.

END