반도체 공정에서의 오염 분석법

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㈜제이케이씨 주 성 경

반도체 공정에서 분석이란?

1. 분석이란 ?

2. 분석의 종류

불량분석 (Failure Analysis) :

SEM,TEM,FIB등 image장비를 이용하여 불량의 형태를 파악

성분분석 (Contamination Analysis) :

ICP/MS, SIMS, GC/MS등의 장비를 이용하여 불량을 발생시킨 성분 파악(Metal, Organic)

대표적인 물성분석 장치

장비	입사광	측정신호	분석깊이	최소분석면적	원리	취득정보
XPS	특성 X-선	광전자	10~100Å	100㎛	광전자의 측정으로 에너지 준위 결정	화학결합상태, 원소분석
UPS	자외선	광전자	수십Å	100㎛	광전자의 측정으로 에너지 준위결정	진동주파수, 화학결합상태
AES	전자	Auger전자	20~60Å	20nm	Auger 전자의 측정에 의한 원소분석	표면원소분석
SIMS	이온	2차이온	50~300Å	1㎛	2차이온에 의한 질량분석	표면층의 고감도 원소분석
ISS	이온	산란이온	1nm	1mm	일정각도로 산란된 이온의 측정	표면 원소분석
SEM	전자	2차전자, X-선	100Å	10Å	가속전자에 대한 2차전자나 X-선	표면의 형상, 원소조성
TEM	전자	투과전자	50Å	10Å	투과전자의 세기에 따른 명암 영상	격자구조, 결함의 관찰
STEM	전자	투과전자, X-선	10Å	3Å	투과전자의 방출 X-선의 영향	미소영역의 화학조성
RBS	He, H입자	산란이온	20~200Å	1mm	후방산란된 이온의 세기 측정	정성, 정량분석
LEED	전자	산란전자	수원자층	수백㎛	표면 2차원 격자에 의한 산란	표면구조, 흡착원자 배열
EPMA	전자	X-선	1㎛	1㎛	특성 X-선에 의한 원소분포	원소 정량
SAM	전자	Auger 전자	10~100Å	0.1㎛	방출된 Auger전자로 영상 구성	화학성분 분포 측정

AES : Auger electron Spectroscopy

SAM : Scanning Auger Microscopy

RBS : Rutherford Backscattering Spectroscopy

XPS : X-ray Photoelectron Spectroscopy (ESCA)

STEM : Scanning Transmission Electron Microscopy

SEM : Scanning Electron Microscopy

표면분석

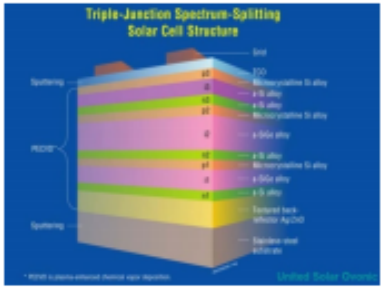
금속 (~ 20Å), 유기물, 고분자물질 (~ 100Å)의 표면과 계면의 구성원소 및 화학적 결합상태, 에너지 준위 등을 알아내는 기술

분석장치의 적용

항 목	수 법
불순물 (주기율표 상 대부분 원소)	**유도결합 플라즈마 질량분석법(ICP-MS)** **Glow 방전 질량분석법(GDMS)** **2차이온 질량분석법(SIMS)** 유도결합 플라즈마 발광분광분석법(ICP-AES) 형관 X선 분석법(XRF)
불순물 (C)	연소-적외선 흡수법 2차이온 질량분석법(SIMS) **Fourier변환적외분광법(FT-IR)**
불순물 (O)	불활성 gas 용융 - 적외흡수법 2차이온 질량분석법(SIMS) Fourier변환적외분광법(FI-IR)
불순물 (H)	불활성 gas 용융 - 열전도도법 2차이온 질량분석법(SIMS)
표면부착물 (이물, 오염, 잔류물등)	비행시간형 2차이온 질량분석법(TOF-SIMS) **유도결합 플라즈마 질량분석법(ICP-MS)** **Ion Chromatography(IC)**
결함, 응력	Cathode luminescence법(CL) Raman 분광법 전자Spin공영법(ESR)
형태관찰	주사전자현미경(SEM) 투과전자현미경(TEM) 원자력간 현미경

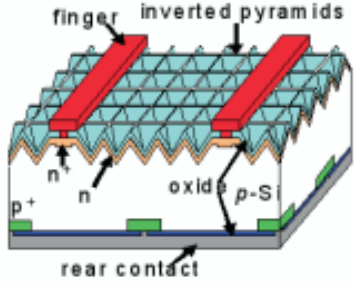
분석장비들의 응용분야

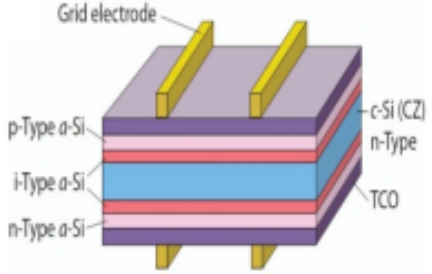
표면 분석
AFM
XPS, AES
TOF-SIMS, SIMS



박막 구조 분석
TEM/STEM, XRD
SEM/EDS, Raman
RBS, FTIR, XRR

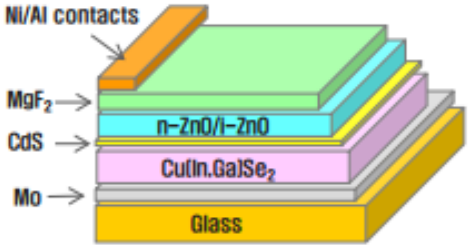
성분 분석
SIMS, GDMS
RBS, AES, XPS
LEXES, XRF





결함 구조 분석
XRD
TEM/STEM
SEM/EDS

오염물질 분석
FTIR, GC/MS
XPS, TOF-SIMS
SIMS, LA-ICP/MS,
AES, SEM/EDS

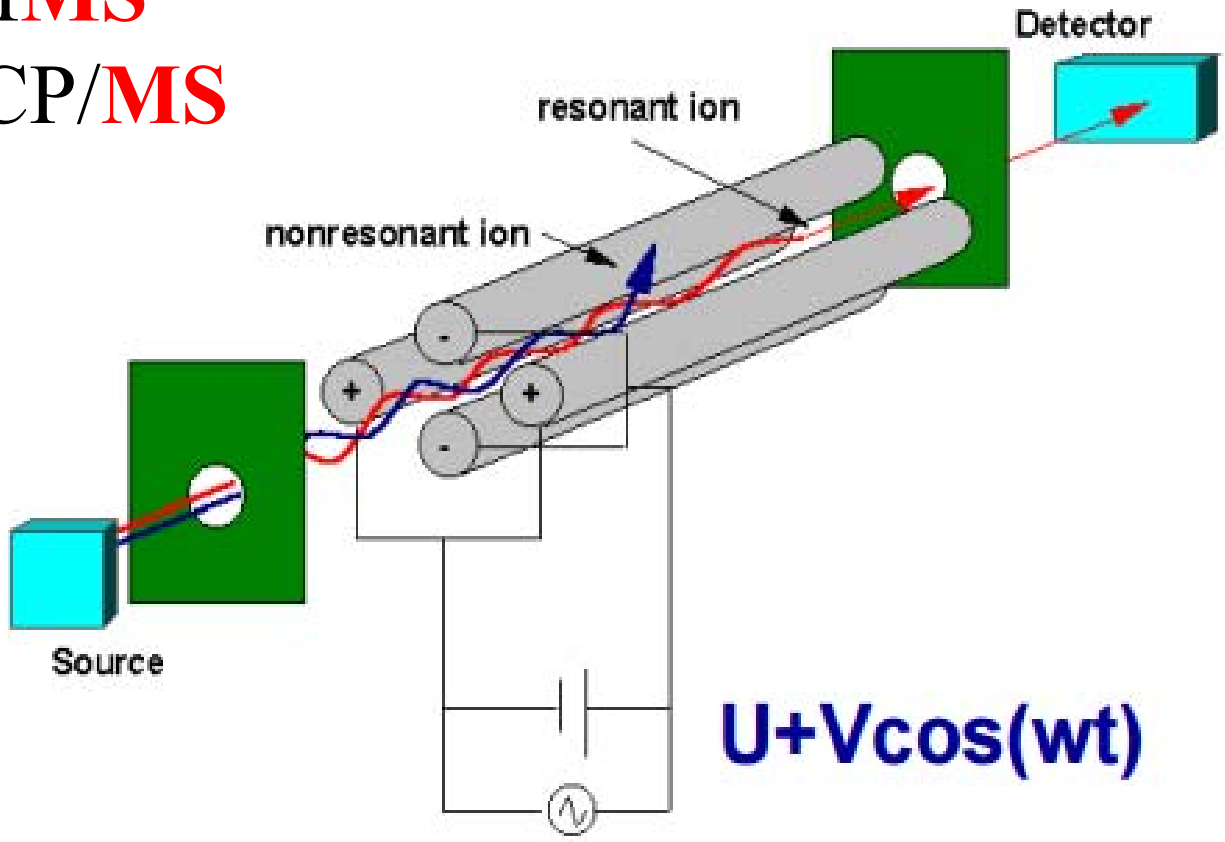


계면 분석
TEM/STEM
SEM/EDS
XPS, AES, SIMS

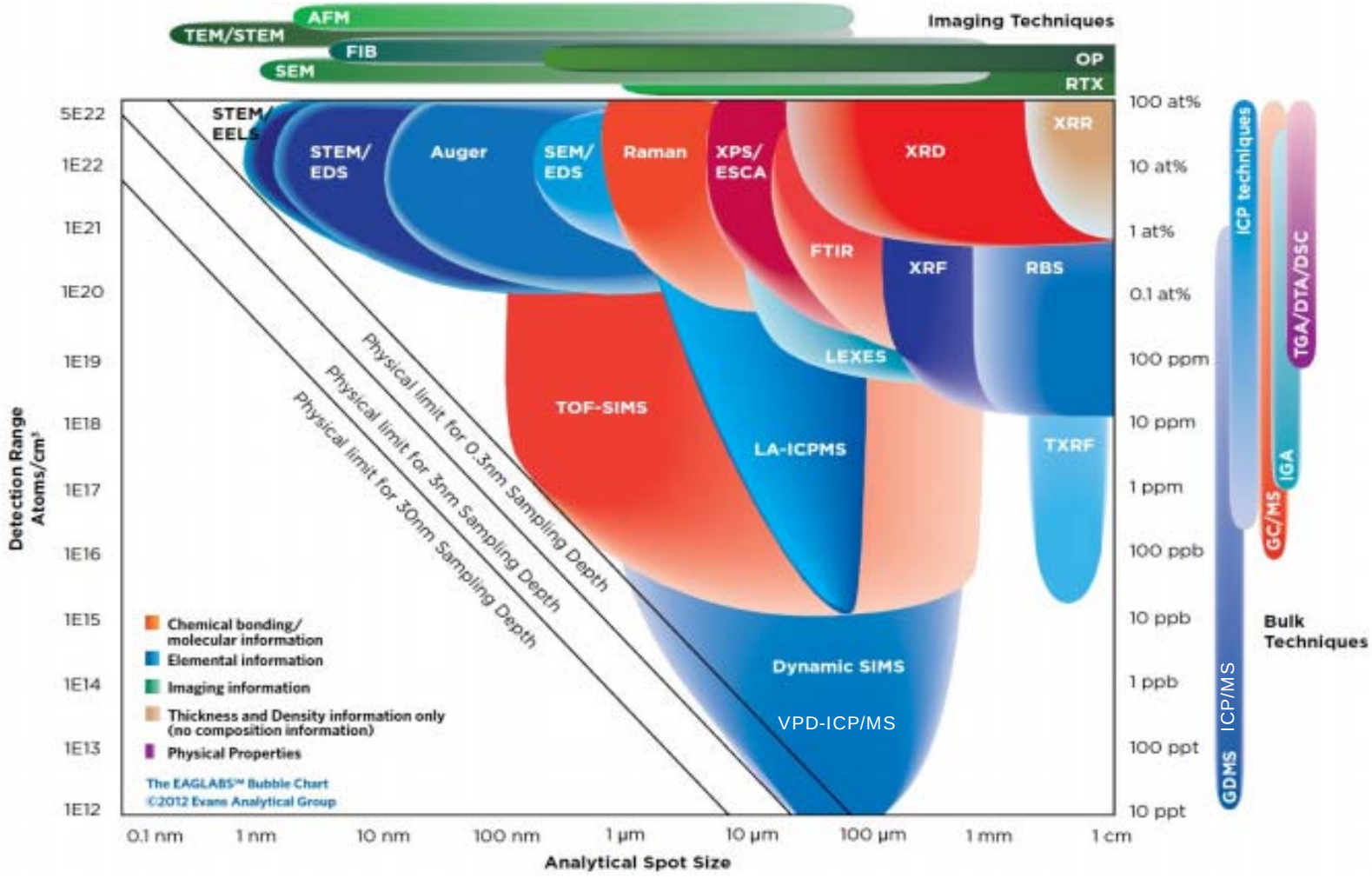
MS(Mass Spectrometry)란?

SIMS

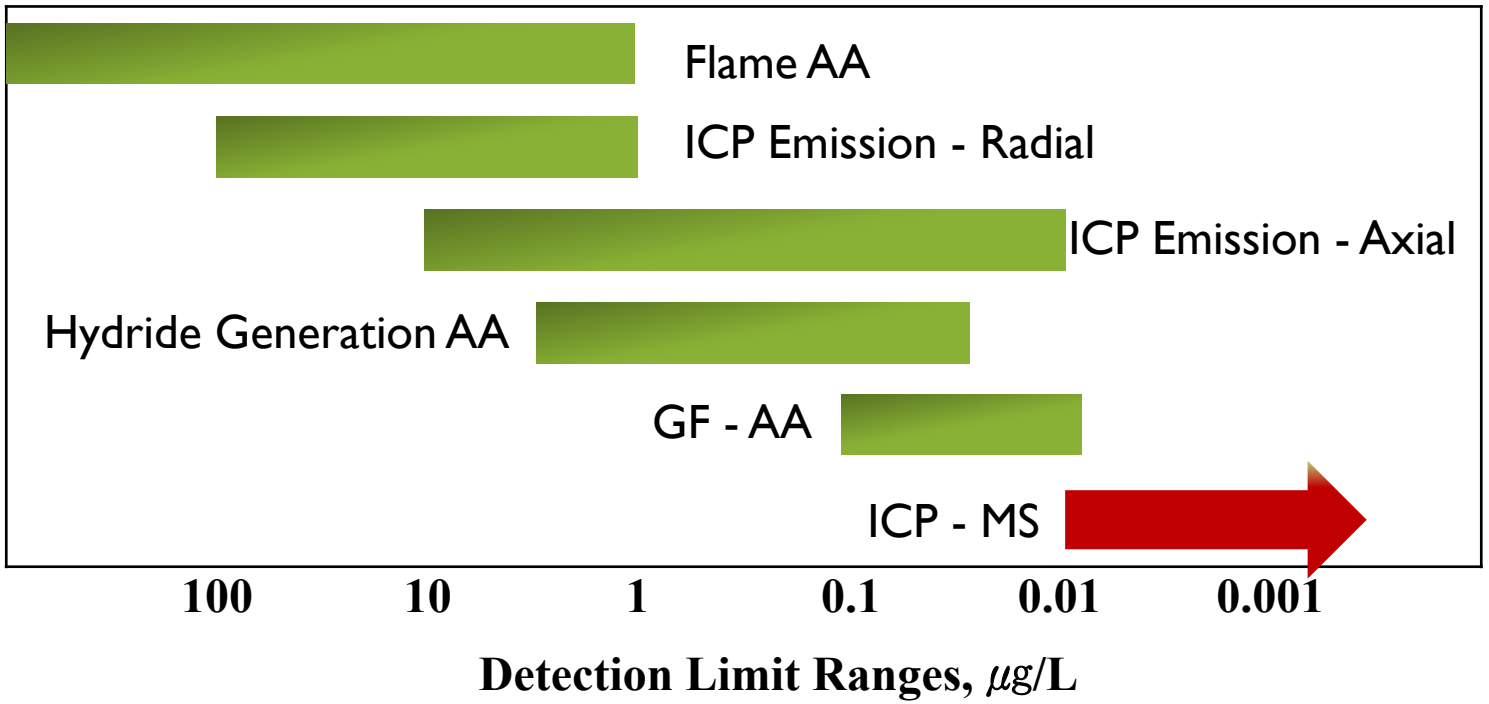
ICP/MS



이차이온질량분석법의 정량범위



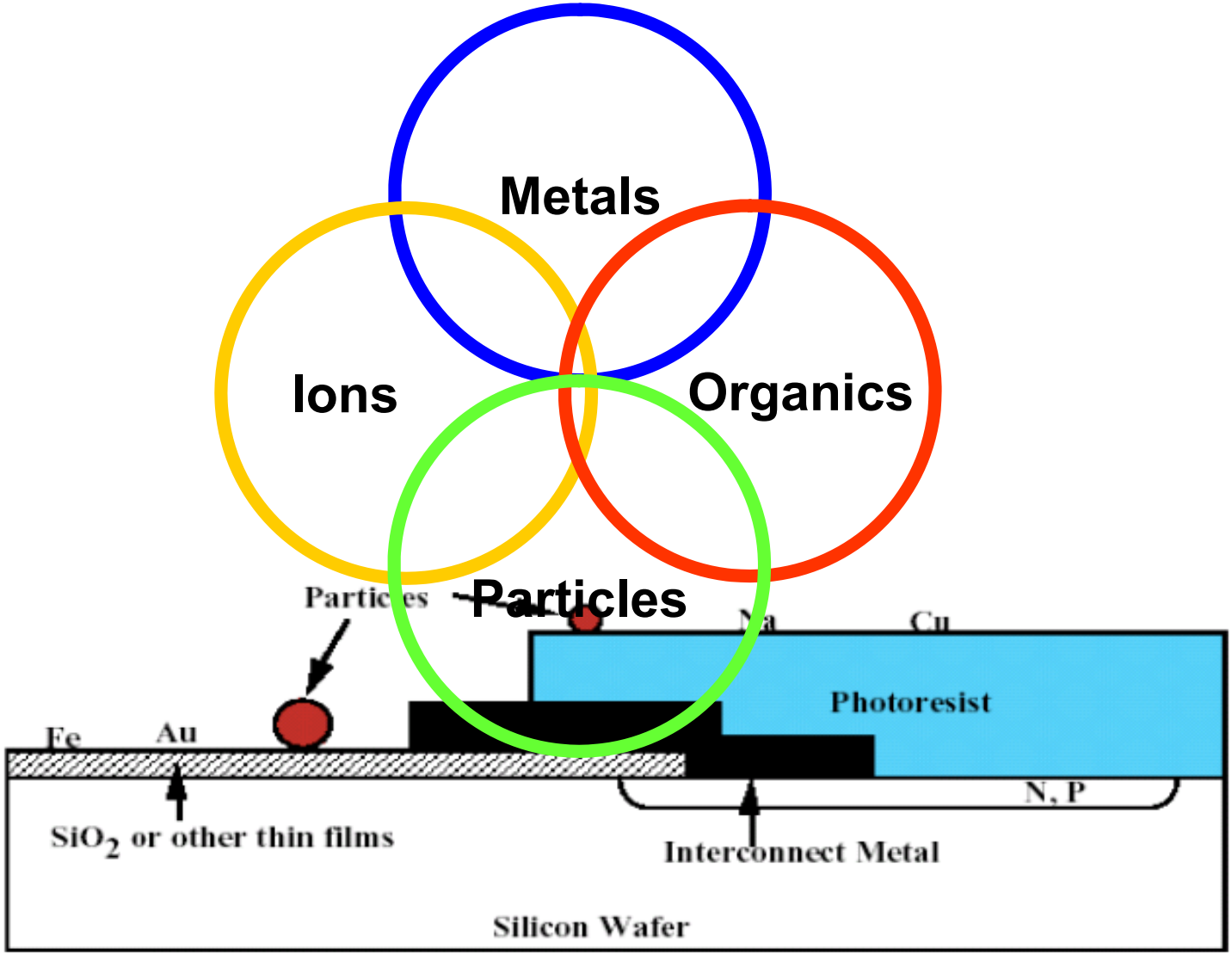
대표적인 금속오염 분석 장비



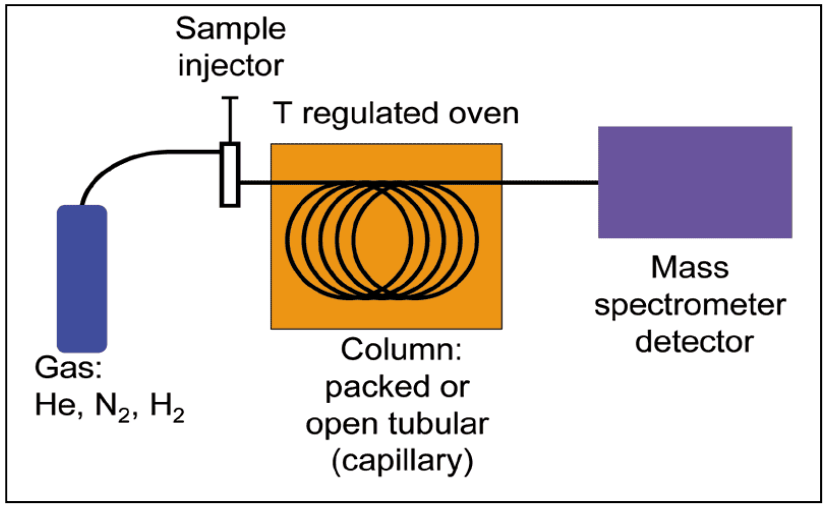
ICP-MS

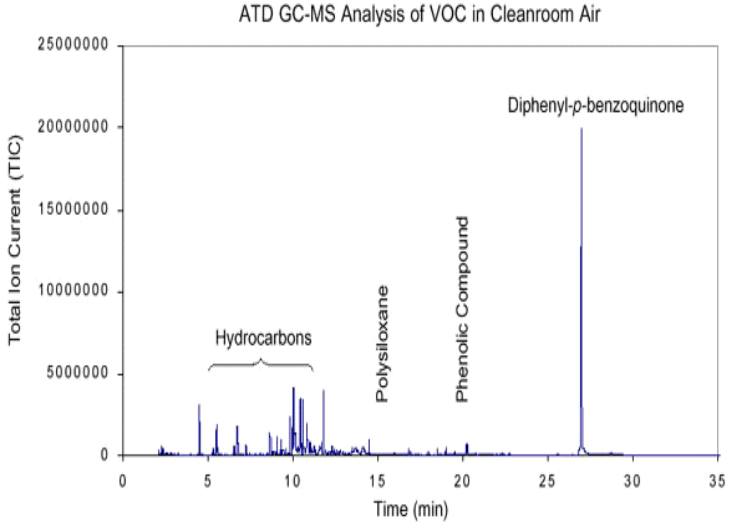
1. 주기율표 상 대부분의 원소 분석 가능
2. 높은 감도
3. 원소분석 + 동위원소 분석 가능
4. 넓은 정량농도 범위
5. 다양한 시료 적용 가능

Contamination 이란?



Organics 분석





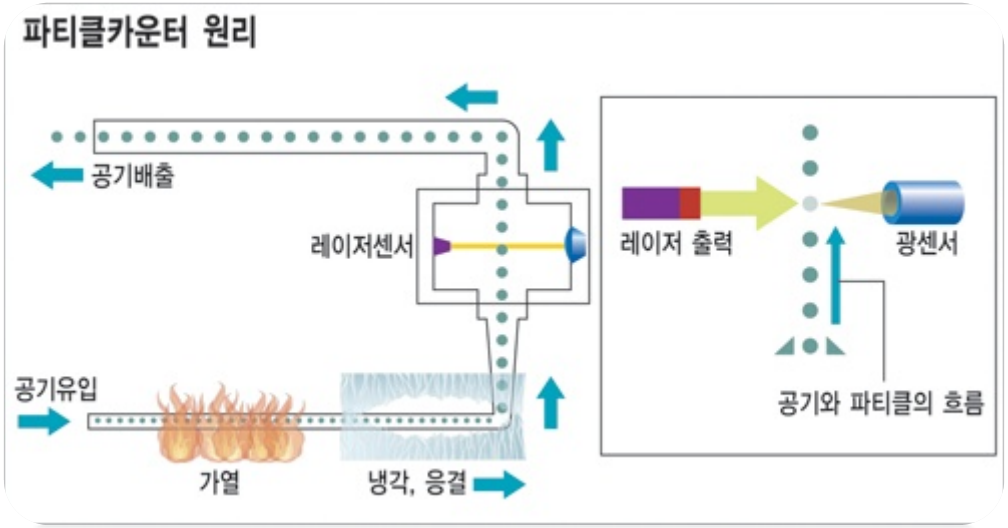
Sample State Analysis Tree

Gas	Liquid		Solid	
GC	GC	NMR	EM	IR
MS	LC	XRF	NMR	Raman
IR	MS	TGA	XRF	TGA
Raman	IR	DSC	XRD	DSC
	Raman			DMA
	UV/Vis			

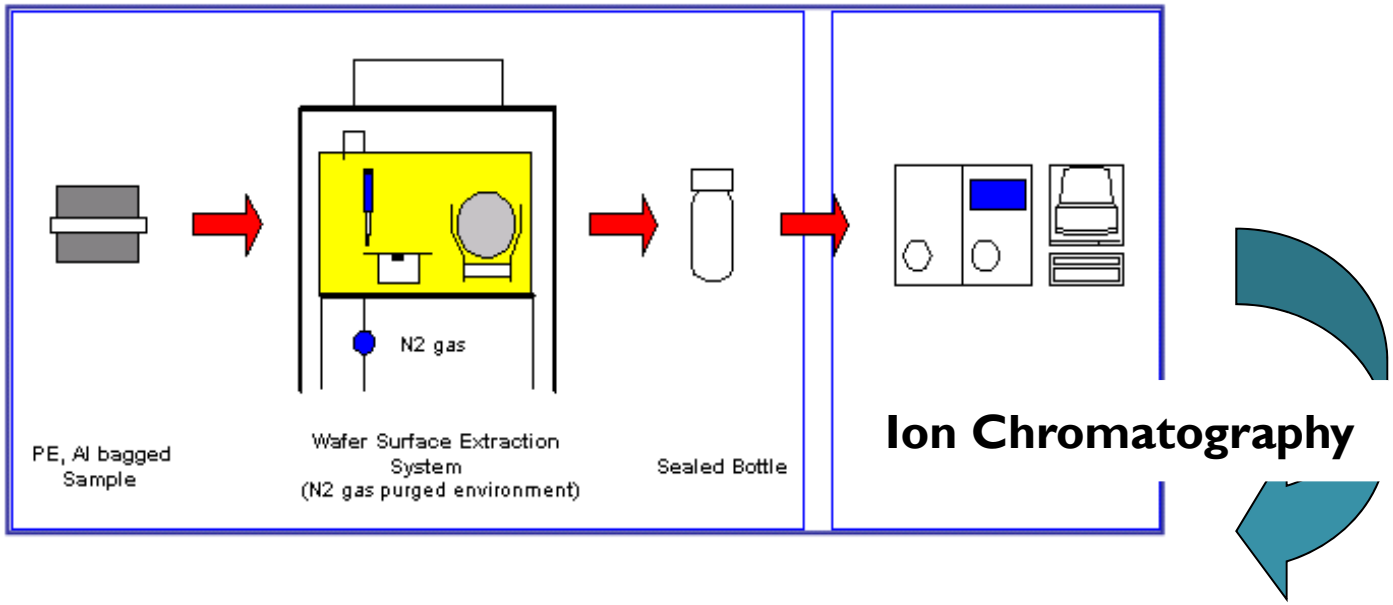
Particles 분석

Contaminant Type	Size (μm)
Human hair	70-100
Human skin flakes	0.4-10
Pollen	5-100
Mold	2-20
Smoke	0.01-1
House dust	0.05-100
Bacteria	0.25-10

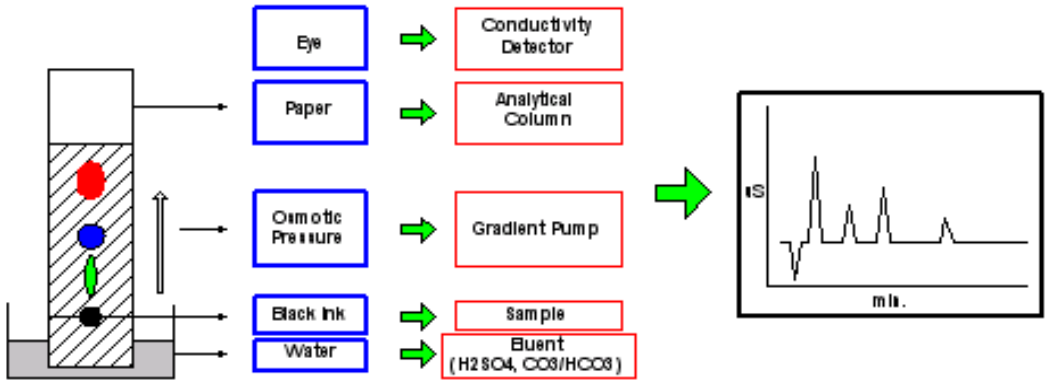
Sizes of a number of common cleanroom contaminants



Ions 분석



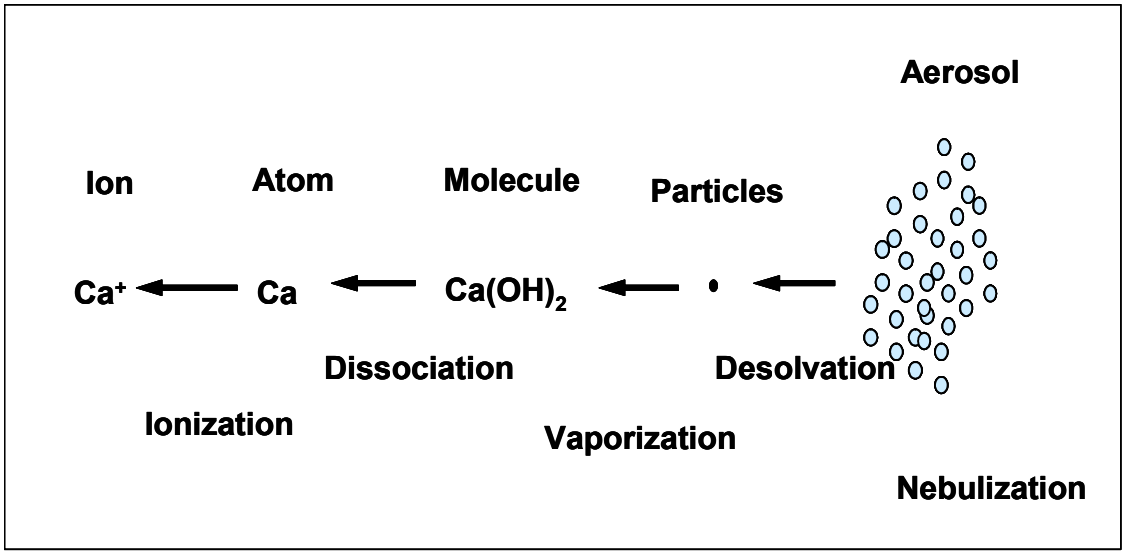
- Wafer Surface (Process Monitoring)
- Cleanroom Ambient Air
- Ultra Pure Water
- High Purity Chemicals

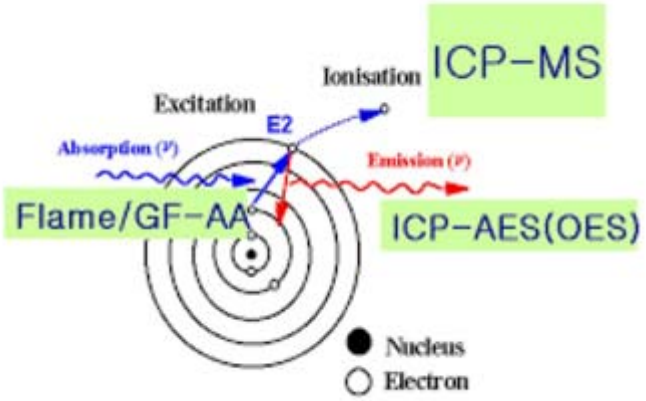


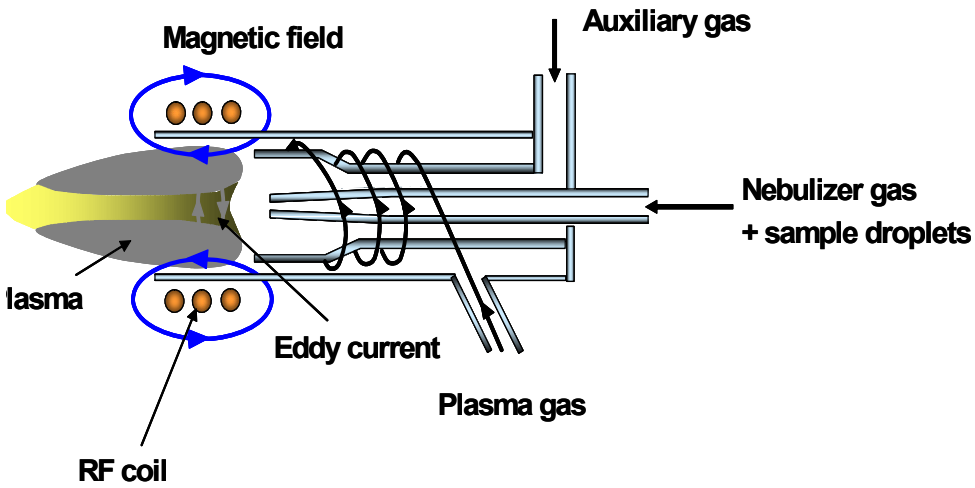
TLC
Paper Chromatography

Ion Chromatography

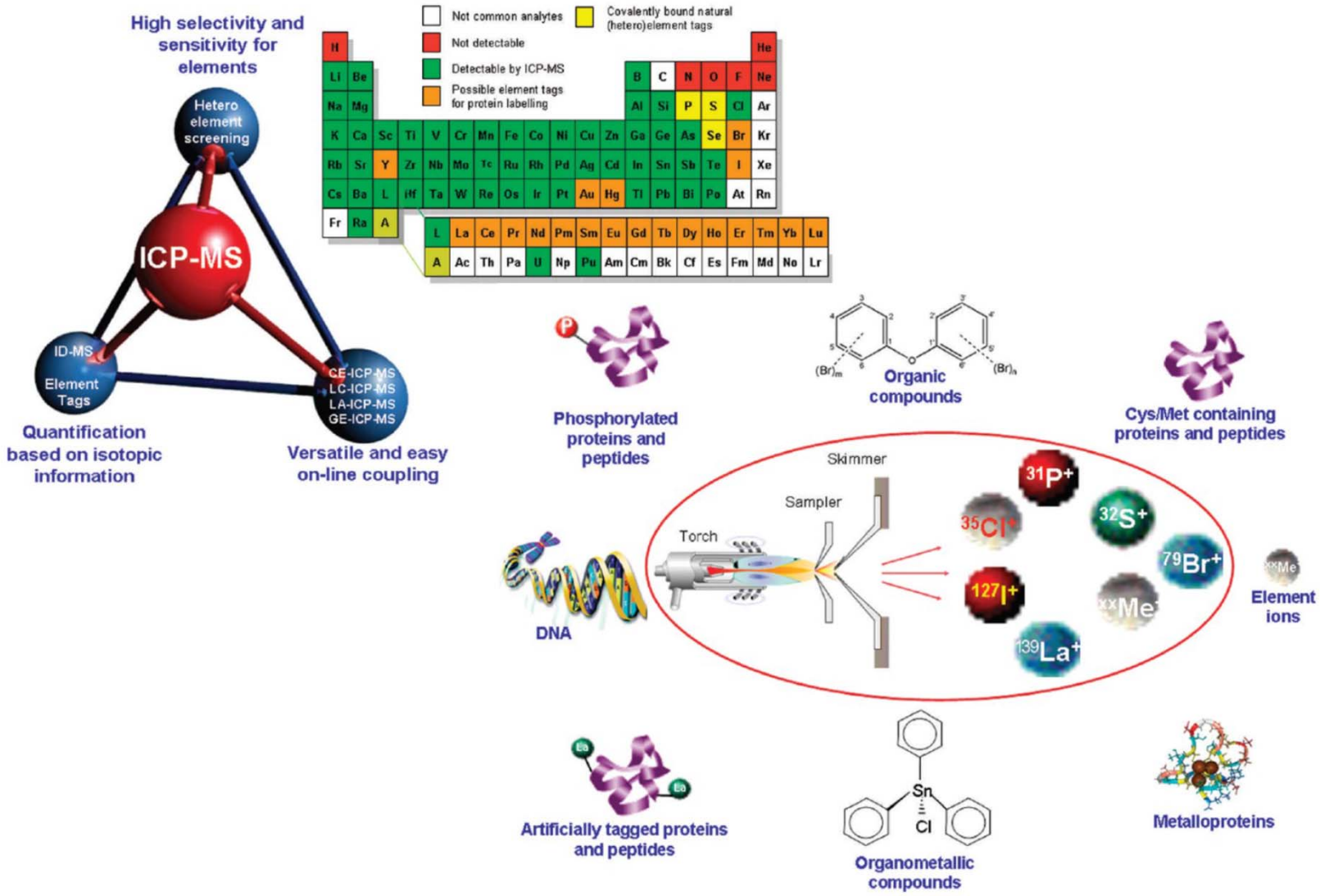
ICP/MS의 원리


Aerosol
Ion
Atom
Molecule
Particles
Ca^+
Ca
$Ca(OH)_2$
Dissociation
Desolvation
Ionization
Vaporization
Nebulization


ICP-MS
Ionisation
Excitation
E2
Absorption (P)
Emission (P)
Flame/GF-AA
ICP-AES(OES)
Nucleus
Electron


Magnetic field
Auxiliary gas
Nebulizer gas
+ sample droplets
lasma
Eddy current
Plasma gas
RF coil

ICP-MS 응용분야의 확대



Surface Metals Analysis Methods

Direct Analysis

Total-Reflection X-Ray Fluorescence (TXRF)

Secondary Ion Mass Spectrometry (SIMS)

Indirect Analysis

Inductively Coupled Plasma Mass Spectrometry (ICPMS)

Graphite Furnace Atomic Absorption Spectrometry (GFAAS)

Surface Extraction Methods

Acid Drop (AD)

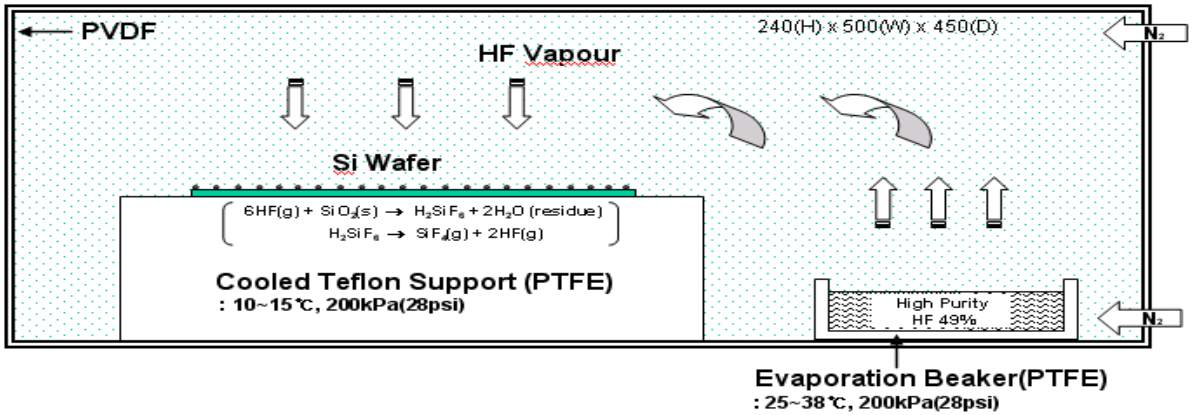
Vapor-Phase Decomposition (VPD)

Analytical techniques for surface metals

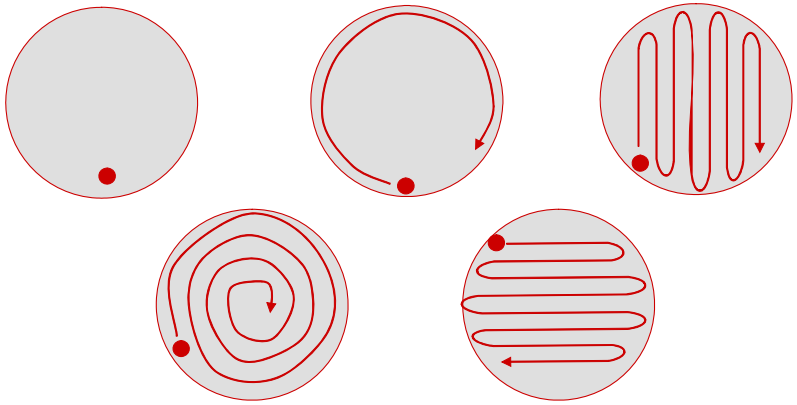
Analytical Technique	Probe In	Detection Out	Detection Depth	Analysis Area (cm^2)	D.L. ($atoms/cm^2$)
ESCA	x-ray	Electron	5 nm	1	10^{13}
N-RBS	Ion	Ion	5 nm	10^{-2}	10^{10}
XRF	x-ray	x-ray	1 μm	1	10^{13}
VPD ICP-MS	Photon	Photon	5 nm	10^{+2}	$10^{8} – 10^{9}$
SIMS	Ion	Ion	5–50 nm	10^{-4}	$10^{9} – 10^{11}$
TXRF	x-ray	x-ray	5 nm	1	$10^{10} – 10^{12}$

ICP/MS를 이용한 Wafer Surface Metals

Vapor-Phase Decomposition (VPD)



Acid drop (AD) extraction



$Fe_2O_3 + 6HF \rightarrow 2FeF_3 + 3H_2O$

$SiO_2 + 6HF \rightarrow H_2SiF_6 + H_2O$

$\xrightarrow{\Delta}$

$H_2SiF_6(s) \rightarrow 2HF(g) + SiF_4$

Extraction solution: 5% HF, 10% H_2O_2 (w/v), Volume: 250 μL.

ICP/MS 분석 단위

ICP/MS등 화학분석 장치는 일차원 단위로 검출됨

〔 ppm(mg/kg), ppb(㎍/kg), ppt(ng/kg), ppq(pg/kg) 〕

ICP/MS정량 범위 : 1ppt이하

1%	0.000,000,00001%
10,000 ppm	0.000,0001 ppm
10,000,000 ppb	0.001 ppb
10,000,000,000 ppt	1ppt

ppt(ng/kg)란 어떤 단위인가?

모래 1개=약 1.5mg

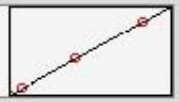
전체 모래량 = 1500ton

1ppt = 모래1개/1500ton

ppt(ng/kg) 분석은 모래사장에서 바늘 찾기……

ICP/MS 분석 단위 환산

ICP/MS Raw data

Label	Mg 279.553 {121}	Cr 283.563 {119}	K 766.490 {44} (A	Co 228.616 {447}	Ca 393.366 {86} (	In 230.606 {446} (
	-0.075	0.000	0.000	0.000	0.000	0.000
TD1	0.987 (1.000)	1.065 (1.000)	0.934 (1.200)	1.050 (1.000)	1.030 (1.000)	1.055 (1.000)
TD2	5.174 (5.000)	5.293 (5.000)	5.143 (5.200)	5.209 (5.000)	5.030 (5.000)	5.168 (5.000)
TD3	9.914 (10.000)	9.847 (10.000)	10.558 (10.500)	9.890 (10.000)	9.982 (10.000)	9.911 (10.000)
alibrations						

Label	Mg 279.553 {121}	Cr 283.563 {119}	K 766.490 {44} (A	Co 228.616 {447}	Ca 393.366 {86} (	In 230.606 {446} (
M_PPM	0.971	1.034	2.895	3.065	5.026	5.037

Atoms/㎠로 환산

Name	Al	Cr	Fe	Ni	Cu	Zn	Na
initial	7.01E+11	4.44E+10	6.97E+11	3.40E+10	1.669E+10	9.28E+10	1.25E+11
1'st	2.34E+10	1.68E+09	1.30E+10	6.72E+08	4.567E+08	1.68E+09	5.73E+09
2'nd	7.32E+09	1.45E+09	1.24E+10	4.73E+08	3.913E+08	6.22E+08	1.11E+09

Sample : 300mm silicon wafer

분석 단위 환산

단위환산 : ppb → atoms/cm^2

$$\text{Surface Concentration } (\text{atoms/cm}^2) = \frac{(C_P - C_B) \times V \times N_A \times 10^{-9}}{MW \times S}$$

Where: C_P = measured concentration (ppb) in the part extract

C_B = measured concentration (ppb) in the solution blank or control

V= volume of the extraction solution (mL)

N_A= 6.023 x 10^{23} (Avagadro's number)

MW = Molecular Weight of the ion analyte of interest

S = extraction surface area (cm^2)

분석 단위 환산 예

단위환산 : ICP/MS결과 (ppb) → Wafer 표면 결과 (atoms/cm^2)

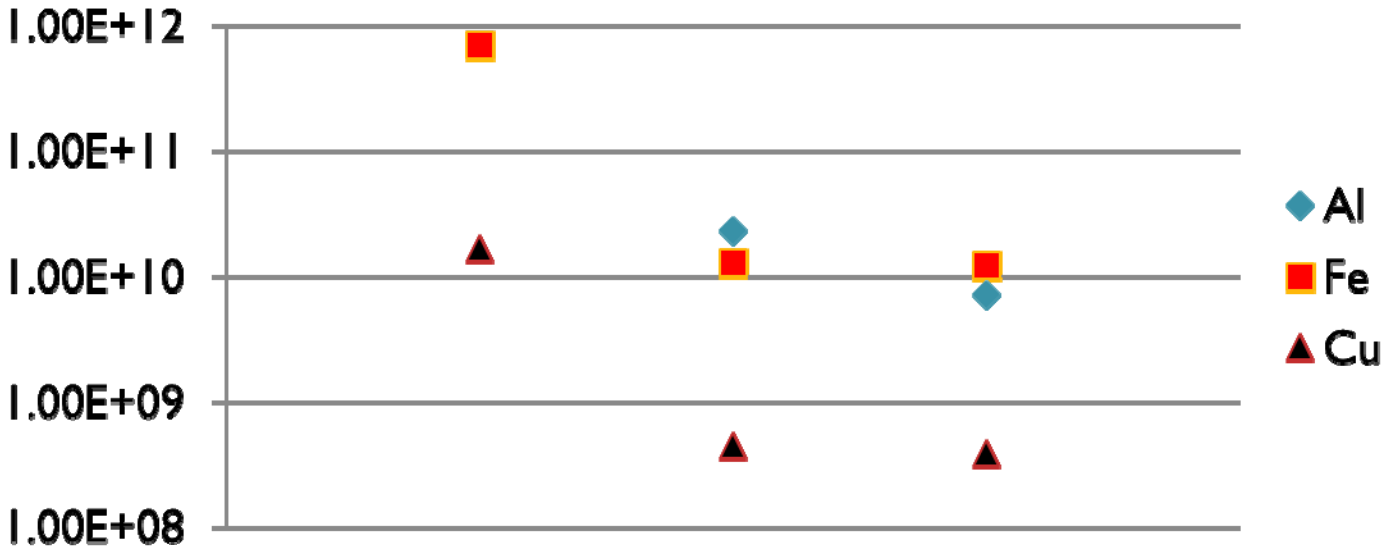
성 분	ICP/MS결과 (ppb=ng/g))	회수액량 (g)	atoms/cm^2
^{27}Al-알루미늄	0.12	2	706.5

분석결과 ng	회수액량 g	Avagadro's no	단위환산 10^{-9}
g		Al 질량(g)	Wafer면적(cm^2)

0.12 ng	2 g	6.023×10^{23}	10^{-9}
g		27 g	706.5 cm^2

* 10^{-9} : 1g =10^{-9}ng

Surface analysis result for 300mm wafer



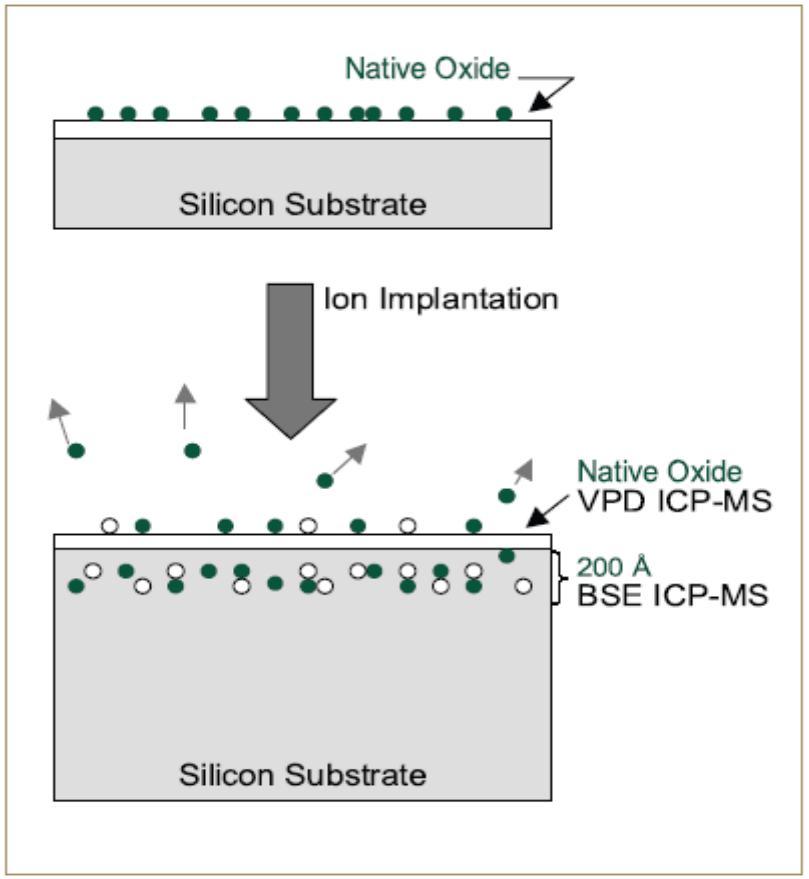
atoms/㎠)

Name	Al	Cr	Fe	Ni	Cu	Zn	Na
initial	7.01E+11	4.44E+10	6.97E+11	3.40E+10	1.669E+10	9.28E+10	1.25E+11
1'st	2.34E+10	1.68E+09	1.30E+10	6.72E+08	4.567E+08	1.68E+09	5.73E+09
2'nd	7.32E+09	1.45E+09	1.24E+10	4.73E+08	3.913E+08	6.22E+08	1.11E+09

Sample : 300mm silicon wafer

VPD ICP-MS application(ion implantation)

KNOCK-ON IMPLANTATION OF SURFACE METALS



BSE ICP-MS CHARACTERIZATION OF AN ARSENIC IMPLANT

BSE ICP-MS	
Element	200 Å
Aluminum	12,300
Antimony	7.3
Boron	230
Chromium	<1
Copper	<1
Iron	<3
Magnesium	<5
Nickel	<0.5
Phosphorous	287
Zinc	1

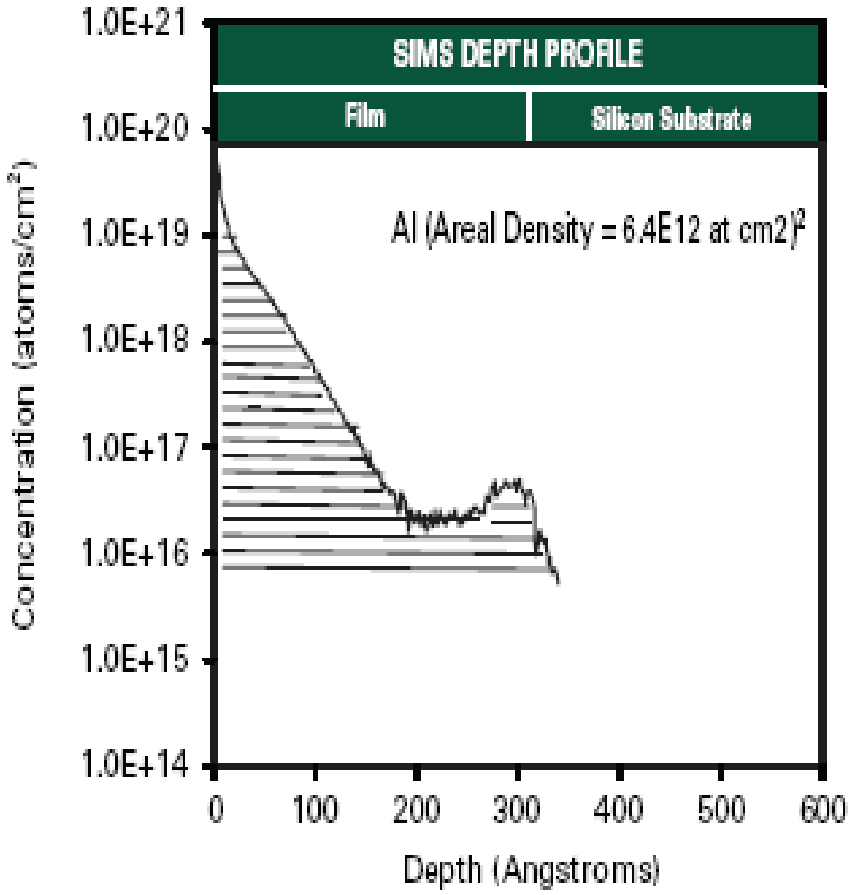
Units: $x10^{10}$ atoms/cm^2

VPD ICP-MS application(PROCESS)

IN-FILM TRACE METAL SURVEY USING DFS ICP-MS

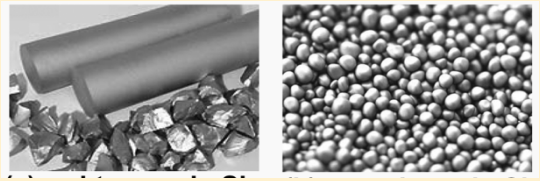
DFS ICP-MS	
Element	**Film**
Aluminum	480
Calcium	<10
Chromium	<2
Copper	29
Iron	19
Magnesium	<10
Nickel	36
Potassium	<10
Sodium	12
Zinc	10
Units: $x10^{10}$ atoms/cm^2	

SIMS DEPTH PROFILE OF THE SAME FILM ANALYZED BY DFS ICP-MS



상온 분해법에 의한 Poly-Si분석 결과

Sample preparation



(a) rod-type (b) granular

Digestion

$$3Si + 18\,HF + 4HNO_3 \rightarrow 3SiF_6H_2 + 4NO\uparrow + 18\,H_2O$$

Dry & cooling

$$SiF_6H_2 + 2HF \rightarrow SiF_4\uparrow + 4\,HF$$

$$4Si + 8HNO_3 \rightarrow Si(NO_3)_2 + 3SiO_2 + \underline{2NH_4NO_3}\downarrow$$

$$2Si(NO_3)_2 + 8HF \rightarrow 2SiF_4\uparrow + 2NO\uparrow + 4H_2O$$

Analysis by ICP-MS

Unit : ppb(ug/kg)

	A	B	C
Na	0.19	0.11	0.16
Mg	0.10	0.11	0.02
Al	0.29	0.55	1.02
K	0.01	0.04	0.18
Ca	0.33	0.18	0.18
Ti	0.22	0.54	0.21
Cr	0.21	0.18	0.18
Mn	0.02	0.04	0.04
Fe	0.59	0.53	0.59
Ni	0.44	0.40	0.45
Cu	0.01	0.01	0.01
Zn	0.07	0.05	0.07
Total (ppb)	2.495	2.721	3.109
순도(%)	99.9999997	99.9999997	99.9999996

$$\text{분석결과(ppb)} = \frac{(\text{ICP/MS결과} - \text{blank}) * \text{용액량(ml)}}{\text{시료량(g)}}$$

감사합니다.

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