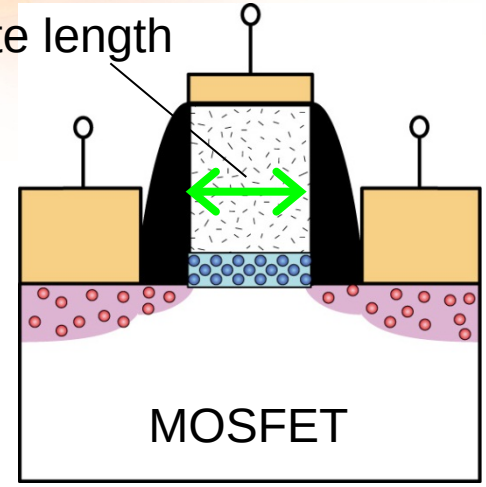
FCMN2013 TU-13 Mar. 26, 2013

# Quantification of Hafnium in Hafnium Oxide Film by Isotope Dilution Neutron Activation Analysis

Toshiko Takatsuka, Kouichi Hirata, Kenji Ito,
Naoko Nonose, Tsutomu Miura

*National Metrology Institute of Japan,*
*National Institute of Advanced Industrial Science and Technology*

# Introduction




Gate dielectric film for Si based transistor

**Hafnium oxide film**

**with high dielectric constant**

**Metrology requirement:**

**4 % in precision 3σ**

| Year | 2011 | 2013 | 2015 | 2017 | 2020 |
|---|---|---|---|---|---|
| Printed Gate length [nm] | 35 | 28 | 22 | 17.7 | 12.5 |
| Equivalent oxide thickness [nm] | 0.88 | 0.79 | 0.67 | 0.55 | – |
| Thickness control EOT %±3σ | <±4 | <±4 | <±4 | <±4 | <±4 |

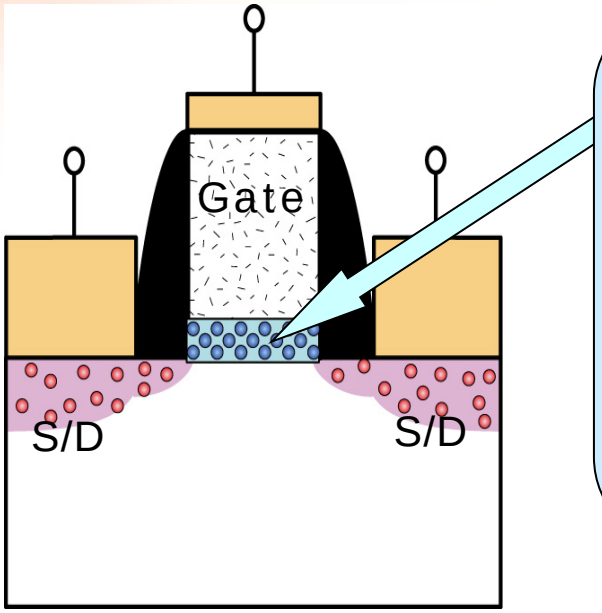
Manufacturable solutions

Known

NOT known

*ref. International Technology Roadmap for Semiconductors 2011*

# Metrology for device process




**Gate dielectric film** thickness??

↓

**Amount of elements**

Neutron activation analysis

X-ray fluorescence

Chemical analysis ( *i.e.* ICP-MS)

Whenever
***reproducible***
***precise***
measurements

+

Wherever
***SI* traceable***
***Reference materials***

=

Higher yield
**&**
Development

***SI**: The International System of Units (abbreviated from the French Le Système International d'Unités)

# Purpose

**Quantification of hafnium in hafnium oxide films by isotope dilution neutron activation analysis**

Accurate measurements of their thicknesses in **length unit** are difficult, possibly caused by the atomic fluctuation at interface layers.

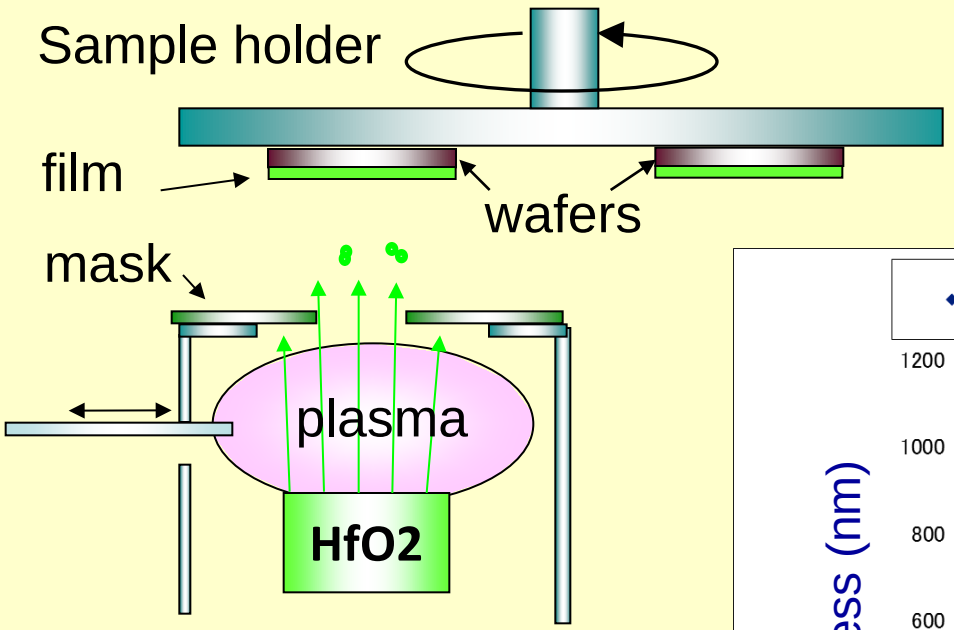
**Quantification in weight unit**

&

Development of ***Certified Reference Materials***

# Hafnium oxide film on Si

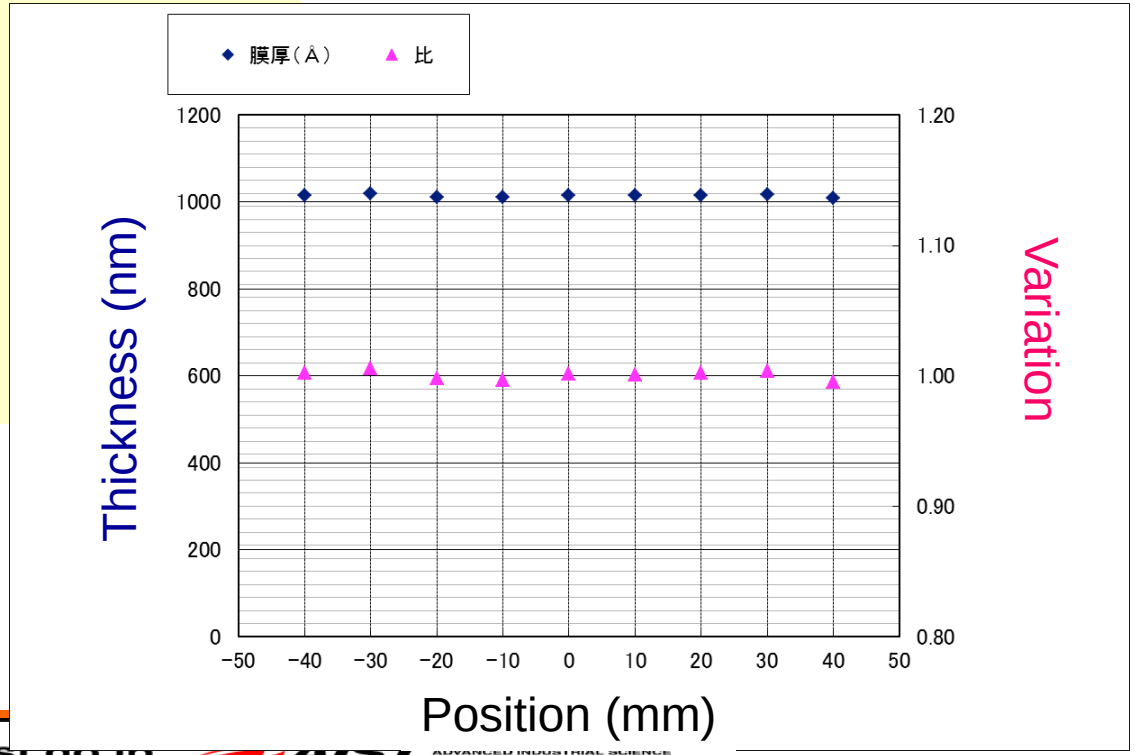
## Magnetron sputtering system




**Thickness uniformity**

**Variation ＜2%**

in 4 inch wafer



# Samples

* Hafnium oxide on Si : 3 samples (unknown)
  Cut a 100 mm wafer into 10×10 $mm^2$ pieces
  Areas were measured by optical scanner

* Hafnium standard solution (known)
  Prepared from NIST SRM 3122

* Hafnium spike solution (unknown)
  Prepared from $^{174}Hf$-enriched hafnium oxide

# Neutron irradiation

All the samples were sealed up separately in clean polyethylene bags. The sealed samples were stacked in a polyethylene container for the neutron irradiation.

$^{180}Hf + n \rightarrow {}^{181}Hf + \gamma$ decay time: 42 days

$^{174}Hf + n \rightarrow {}^{175}Hf + \gamma$ decay time: 60 days

## Irradiation

Pn-2 in the Kyoto university research reactor (KUR)
4 hours with a $5.5 \times 10^{12}$ $cm^{-2} \cdot s^{-1}$ thermal neutron fluence rate

# Quantification of hafnium

## Isotope dilution : ID

**$HfO_2$**

Hf in $HfO_2$ film
$W_{nat}$ (g)

isotopic composition
[ $K_{nat,174}$ , $K_{nat,180}$ ]

**spike**

Hf
$W_{sp}$ (g)

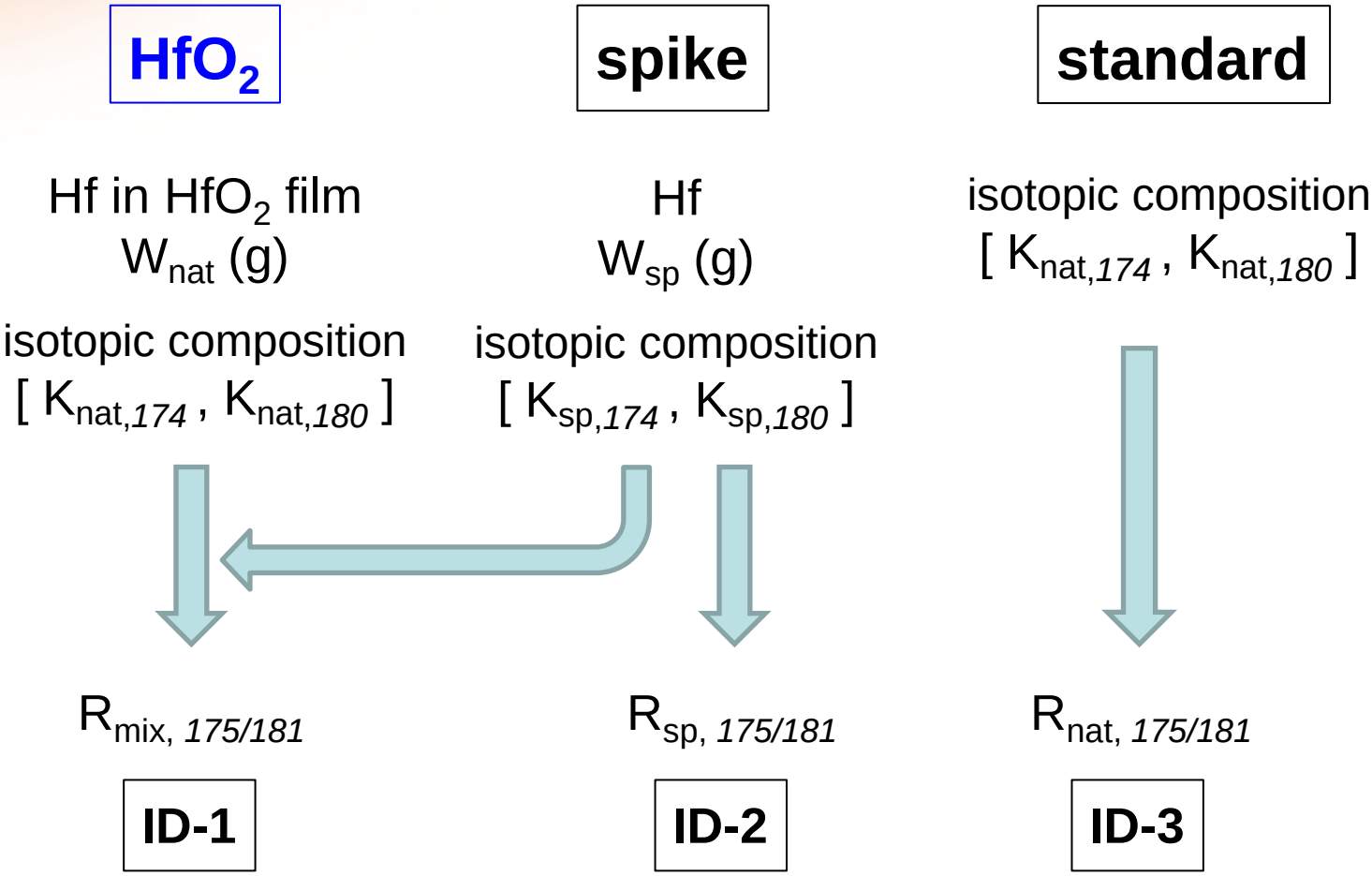
isotopic composition
[ $K_{sp,174}$ , $K_{sp,180}$ ]

**standard**

isotopic composition
[ $K_{nat,174}$ , $K_{nat,180}$ ]

| Atomic mass | 174 | 180 | |
|---|---|---|---|
| natural | 0.16 % | 35.08 % | IUPAC2001 |
| spike | 19.01 % | 18.97 % | $^{174}$Hf enriched |

# ID




ref. Yonezawa et al., *Anal. Chem.* **55**, 2059-2062 (1983).

# reverse-ID

**spike solution**

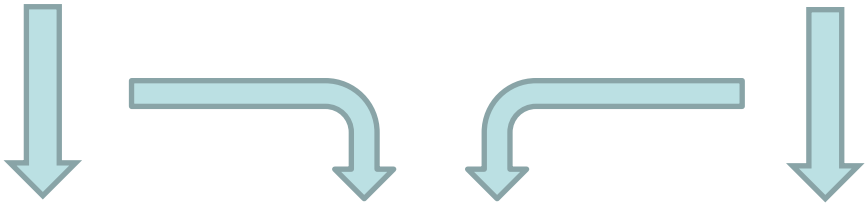
Hf
$W_{sp}$ (g)

isotopic composition
[ $K_{sp,174}$ , $K_{sp,180}$ ]

**standard solution**

Hf
$W_{nat}$ (g)

isotopic composition
[ $K_{nat,174}$ , $K_{nat,180}$ ]



$R_{sp,\ 175/181}$

$R_{mix,\ 175/181}$

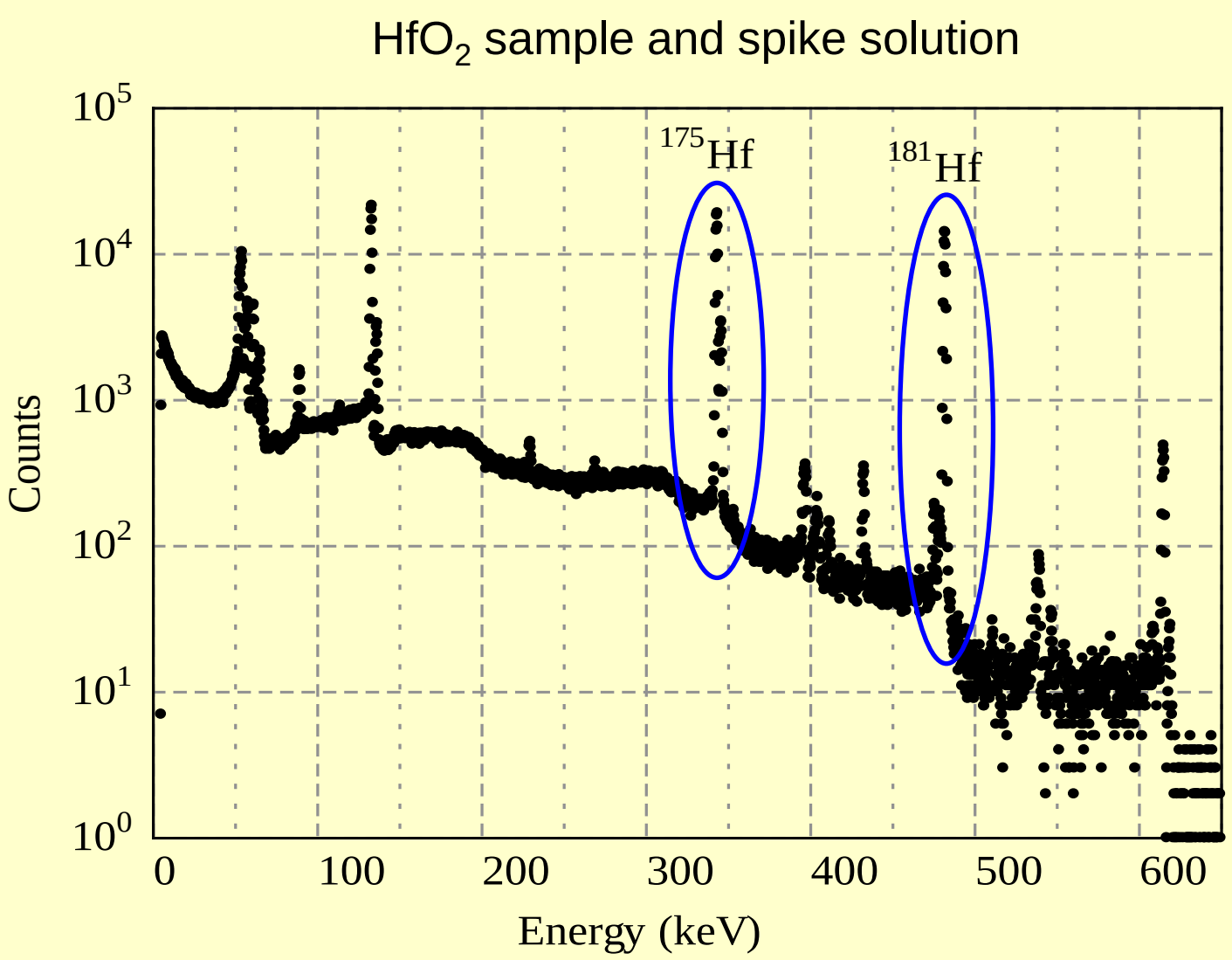
$R_{nat,\ 175/181}$

**ID-2**

**R-ID**

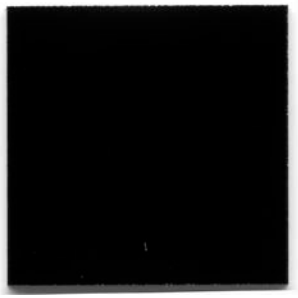
**ID-3**

# Gamma-ray spectrum



# Quantification of hafnium

- Hf amounts were calculated from the results by ID & reverse ID
- Areas were calculated from the image



Optical image of the sample surface

## Analytical results

| | Hf (μg) | Area ($mm^2$) | Hf area density ($\mu g/cm^2$) |
|---|---|---|---|
| HfO2 -1 | 3.591 | 97.63 | 3.679 |
| HfO2 -2 | 3.585 | 97.42 | 3.680 |
| HfO2 -3 | 3.600 | 98.13 | 3.668 |

# Summary

* Hafnium amounts in hafnium oxide films were quantified as area densities through ID-NAA.

* The results demonstrated that ID-NAA is applicable for the precise methodology for semiconductor-device manufactures.

Acknowledgements

The NAA measurements were performed at the facilities of the Research Reactor Institute, Kyoto University.