

# Study of silicon nanodot formation in pulsed-gas plasma process

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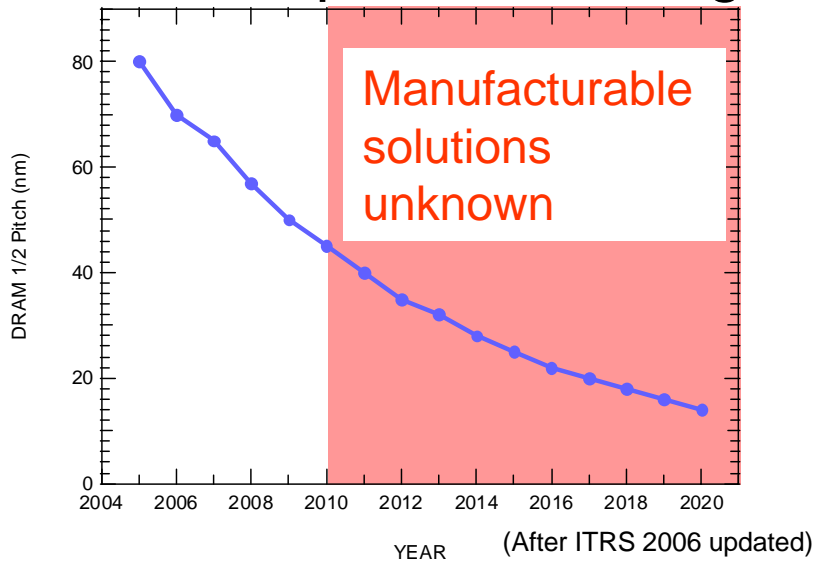
*and*

*SORST, Japan Science and Technology Agency (JST)  
Tokyo, JAPAN*

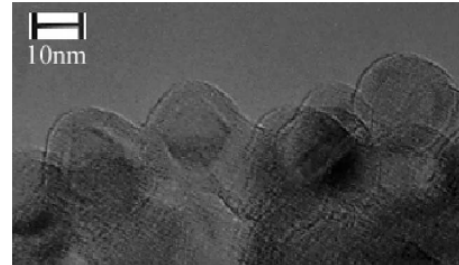
# Introduction

## Future Silicon Nanodevices

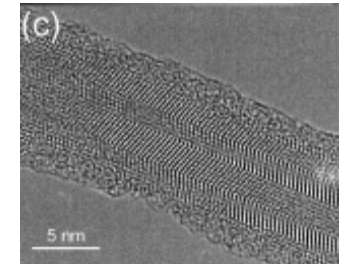
Limit of top-down scaling → Use of bottom-up nanostructures



Silicon nanodot



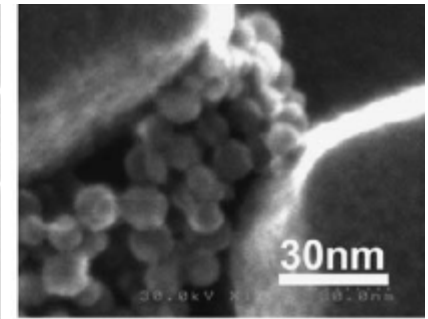
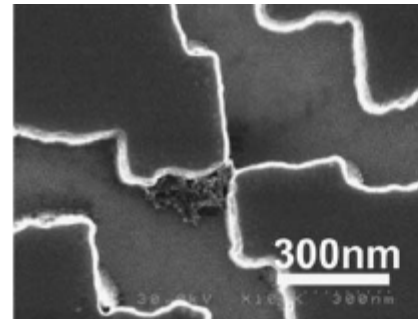
S. Oda,  
Mat. Sci. Eng. **B101**, 19 (2003).



S. Hofmann *et al.*,  
J. Appl. Phys. **94**, 6005 (2003).

Silicon nanowire

Fusion of top-down and  
bottom-up technologies



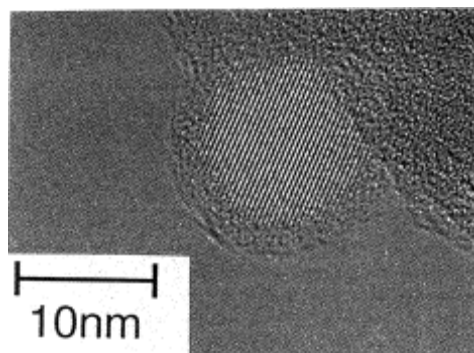
A. Tanaka *et al.*, Curr. Appl. Phys. **6**, 344 (2006).



Open a new field of silicon nanodevices

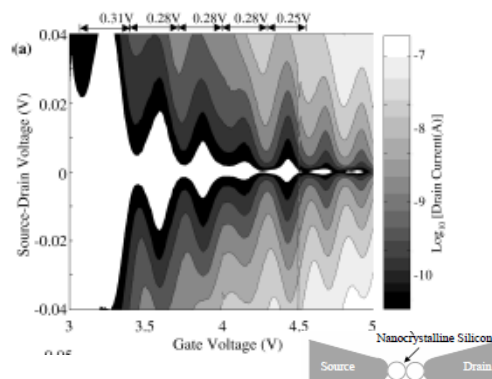
# Silicon nanodots (SNDs)

Key building block for future Si nanodevices

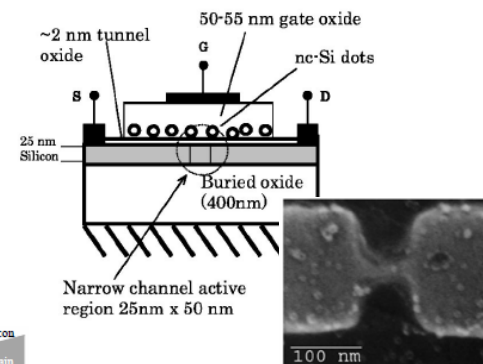


T. Ifuku *et al.*, Jpn. J. Appl. Phys. **36**, 4031 (1997).

## Single Electron Transistor/Memory

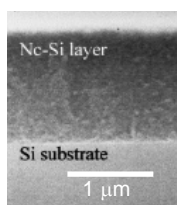


A. Dutta *et al.*,  
Jpn. J. Appl. Phys. **39**, 4647 (2000).

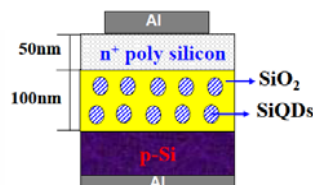
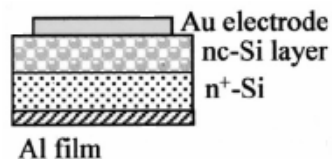


B. J. Hinds *et al.*,  
J. Appl. Phys. **90**, 6402 (2001).

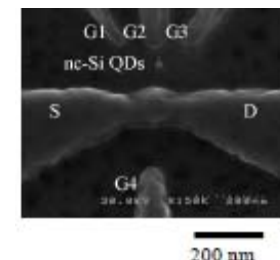
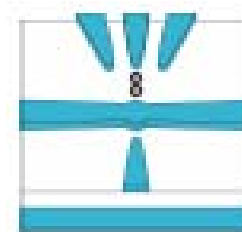
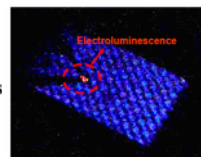
## Electron/Light Emitter



K. Nishiguchi *et al.*,  
J. Appl. Phys. **92**, 2748 (2002).



H. Cheong *et al.*,  
Tech. Dig. CLEO 2006 CTuN4 (2006).

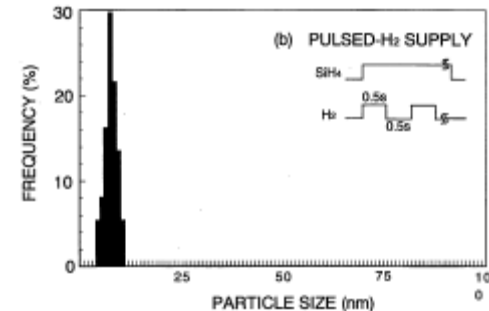
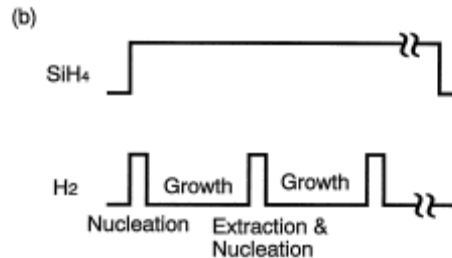
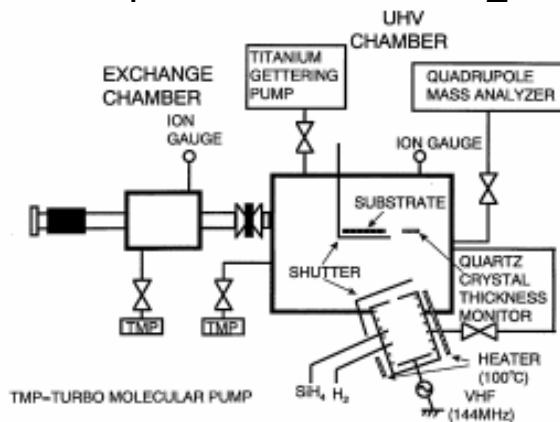


Y. Kawata *et al.*, Ext. Abst. SSDM 2006, pp. 812 (2006).

# SNDs Fabrication – Pulsed Gas VHF Plasma Process

$\text{SiH}_4$  Plasma +  $\text{H}_2$

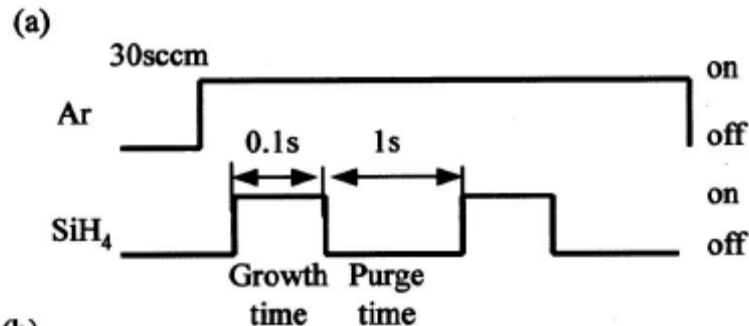
T. Ifuku *et al.*, Jpn. J. Appl. Phys. **36**, 4031 (1997).



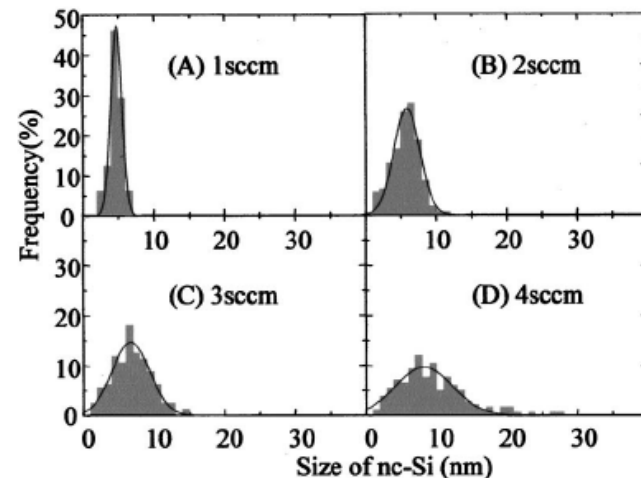
- Nucleation and growth time control
- Diameter around  $8 \pm 1$  nm achieved

Ar Plasma +  $\text{SiH}_4$

K. Nishiguchi *et al.*, J. Appl. Phys. **92**, 2748 (2002).

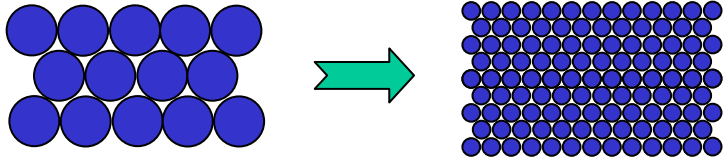


- Faster deposition rate with keeping mono-dispersion



## Technical challenge

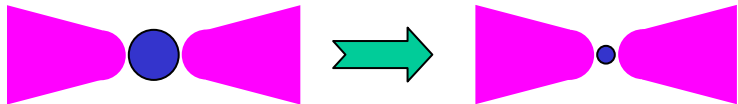
## Further miniaturization



High density assembly

Large  $\Delta V_{th}$  for non-volatile memory

High efficiency in electron emitter



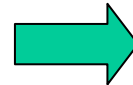
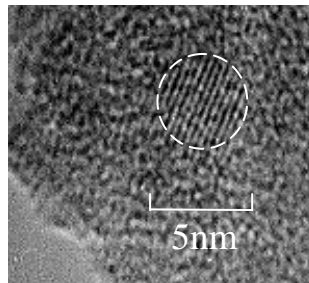
Increasing charging and quantum confinement energies

High temperature operation of SET or quantum information devices  
Blue shift of emitting light wavelength

## Surface oxidation

(750 °C 15hs)

J. Ohmachi *et al.*,  
Mat. Res. Soc. Symp. Proc. **638**,  
F5.3 1-6 (2001).



In situ growth of small  
SNDs with higher  
deposition rate is  
preferable

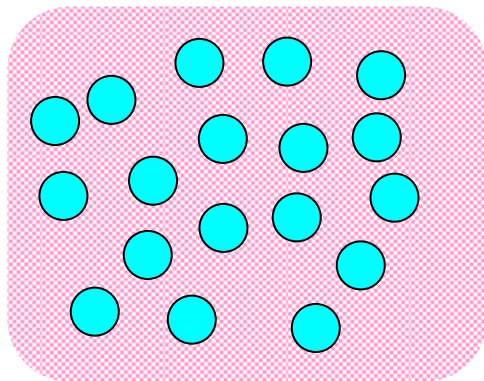
Thick oxide surrounded

# Objective

Toward further miniaturization of SNDs

We study effects of  $H_2$  introduction to the SNDs growth in the pulsed  $SiH_4$  supply to VHF Ar plasma system

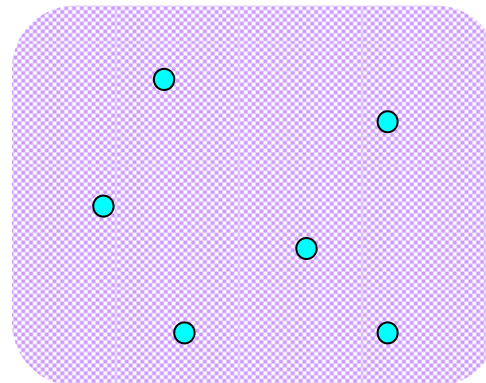
Pulsed  $SiH_4$  in Ar plasma



High deposition rate



Pulsed  $H_2$  in  $SiH_4$  plasma



Mono-dispersed  
with smaller diameter

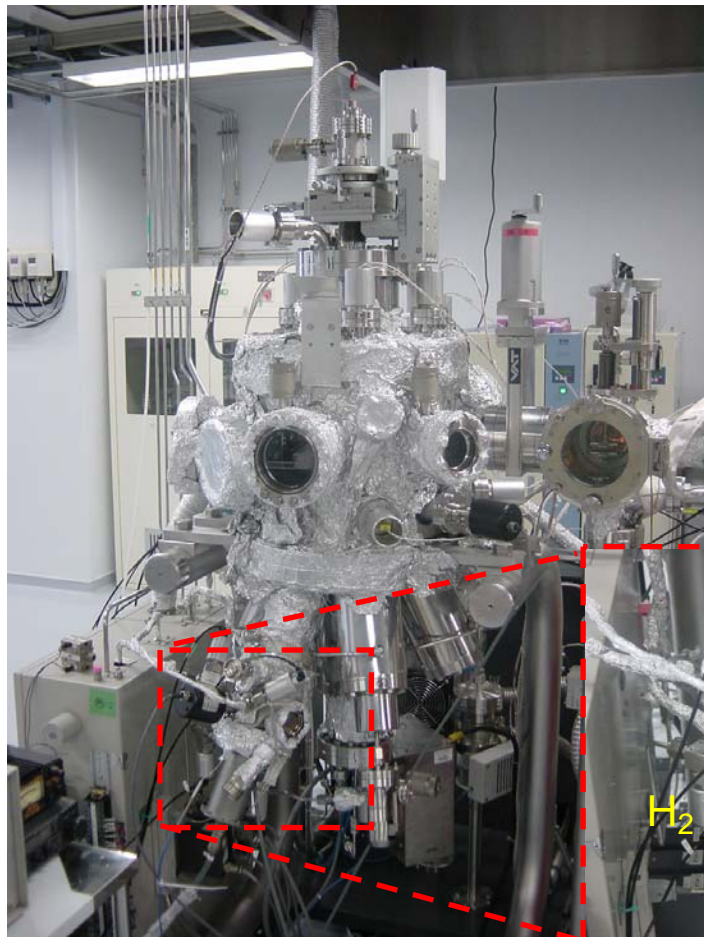
Investigation of SND growth mechanism in  $SiH_4/H_2/Ar$  chemistry



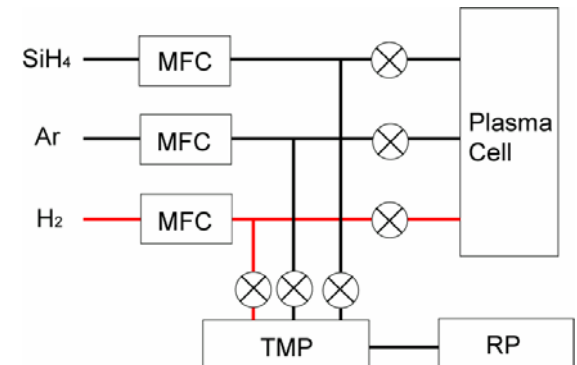
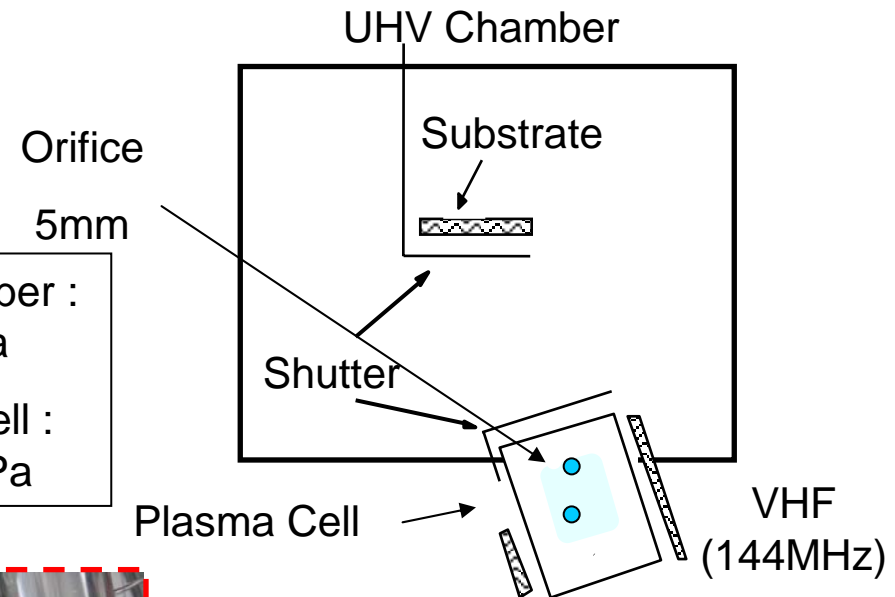
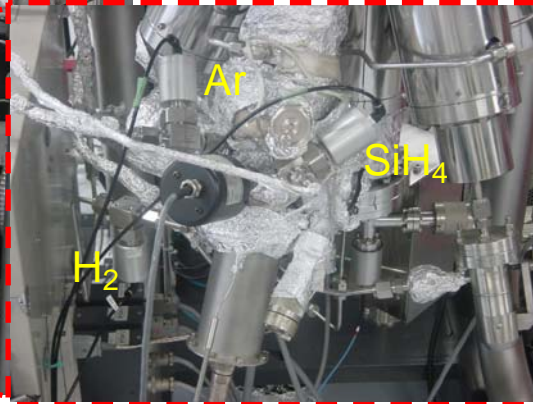
# Experimental

## Apparatus

— Newly introduced deposition chamber

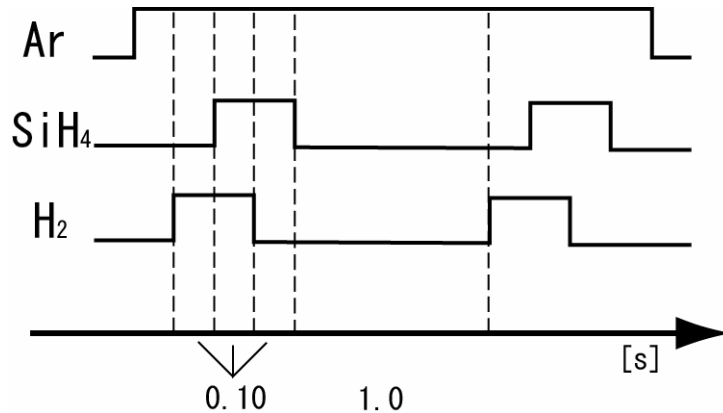


UHV Chamber :  
1-10 Pa  
Plasma Cell :  
10-100 Pa

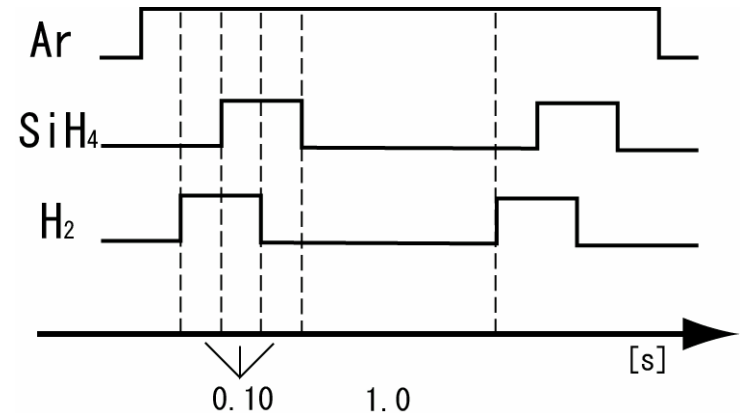


## Gas supply conditions

Pulsed  $\text{SiH}_4$  and Pulsed  $\text{H}_2$   
in Ar plasma



Pulsed  $\text{SiH}_4$   
in Ar/ $\text{H}_2$  plasma



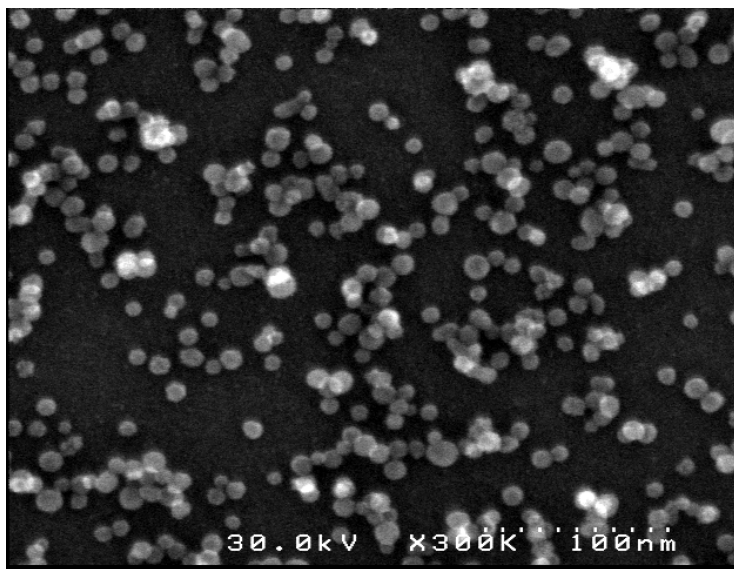
## Observations

Shape, Size – SEM (Hitachi S-5000)  
Crystal or Amorphous – TEM



# Results

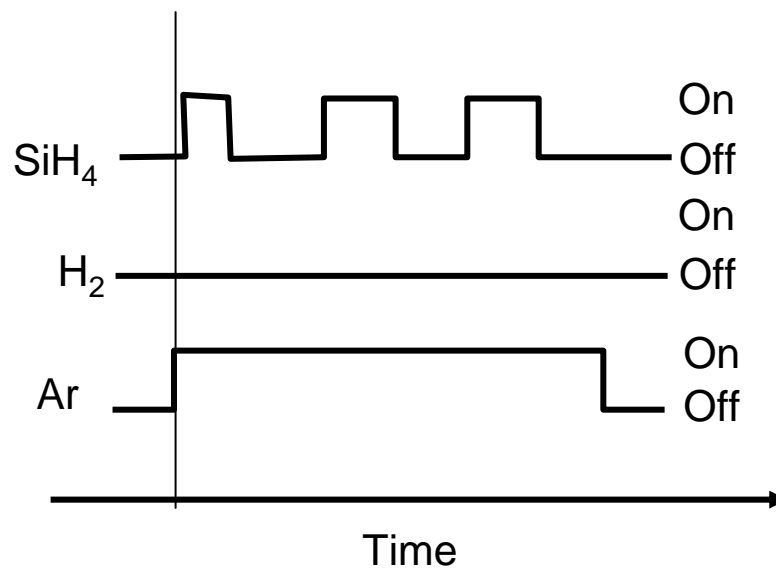
## Pulsed $\text{SiH}_4$ supply to Ar plasma



Spherical SNDs observed

Single crystallized

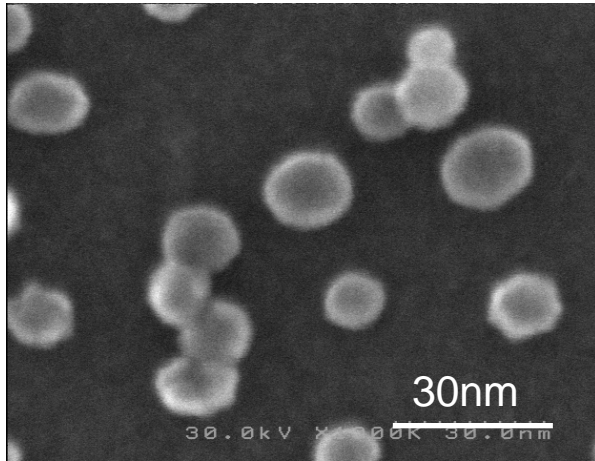
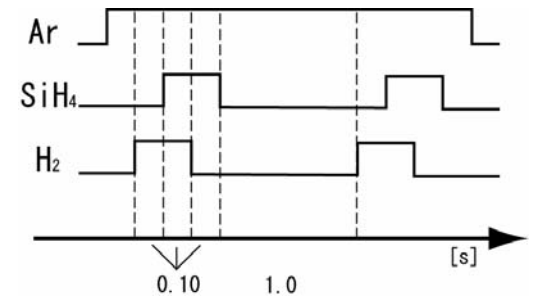
— w/o adding  $\text{H}_2$



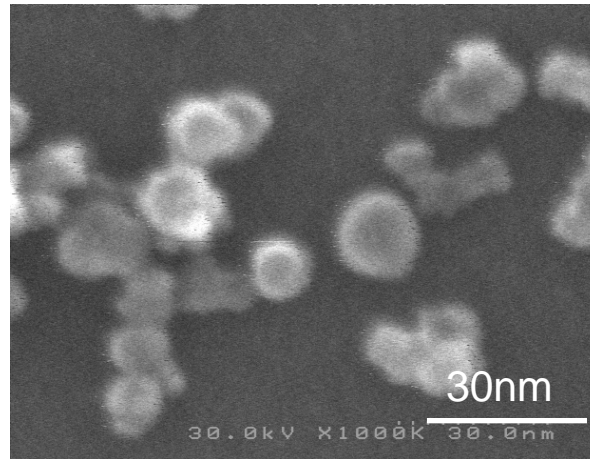
# Addition of Pulsed $\text{H}_2$ Supply

SEM images

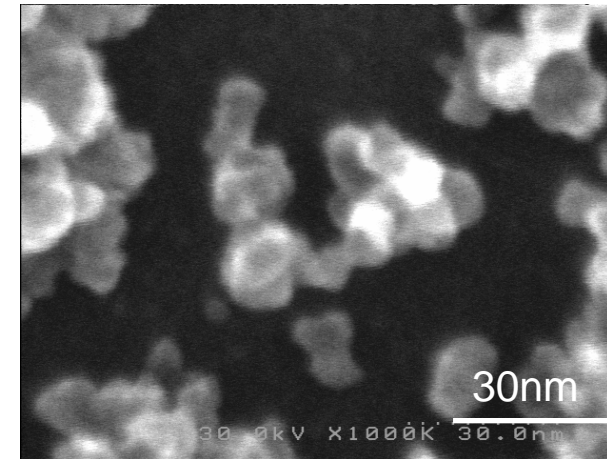
$\text{SiH}_4$  1 sccm Ar 90 sccm



$\text{H}_2$  0.5 sccm

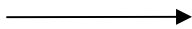


$\text{H}_2$  1 sccm



$\text{H}_2$  20 sccm

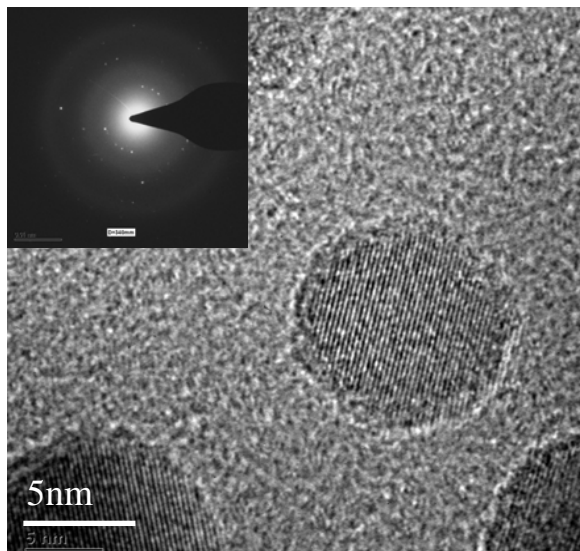
With increasing  $\text{H}_2$  flow rate



- Number of aggregated clusters increases
- Size of individual dots tends to decrease

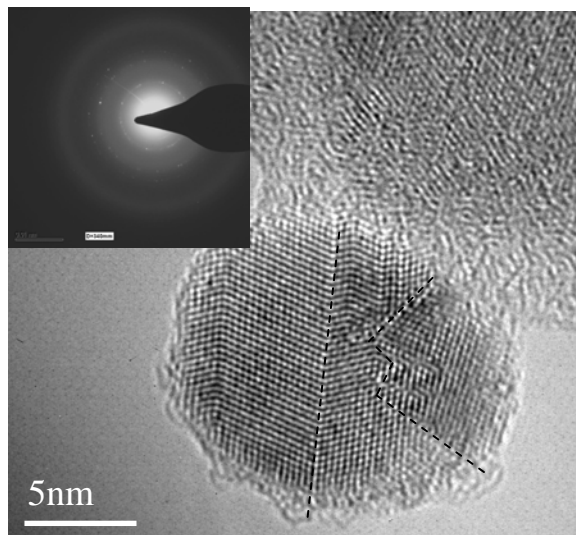
# Addition of Pulsed H<sub>2</sub> Supply

\_\_\_\_\_ TEM images



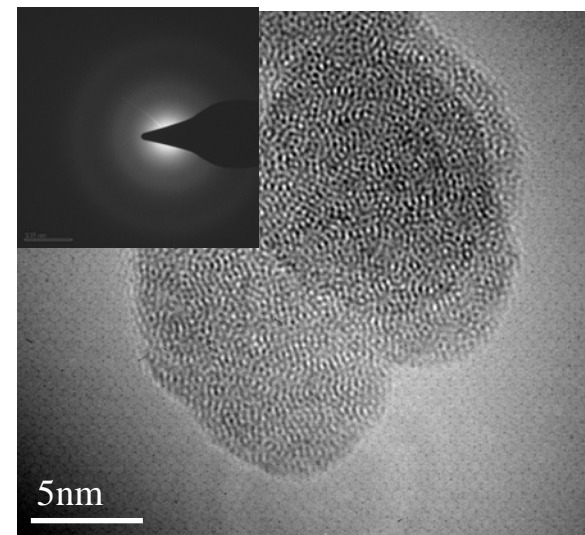
H<sub>2</sub> 0.5 sccm

Single-crystalline



H<sub>2</sub> 1 sccm

Poly-crystalline



H<sub>2</sub> 20 sccm

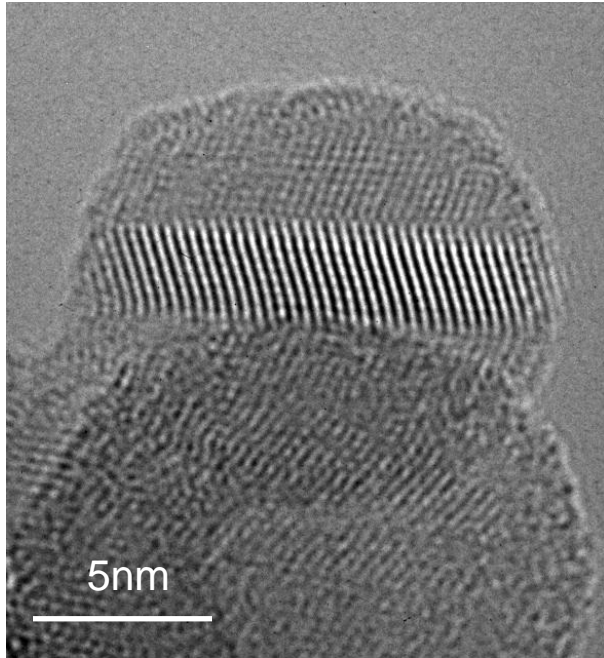
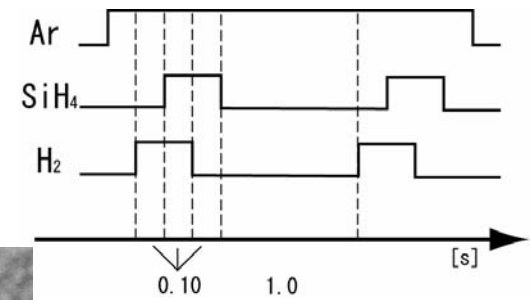
Amorphous

————→ Crystallinity decreases with increasing H<sub>2</sub> flow rate

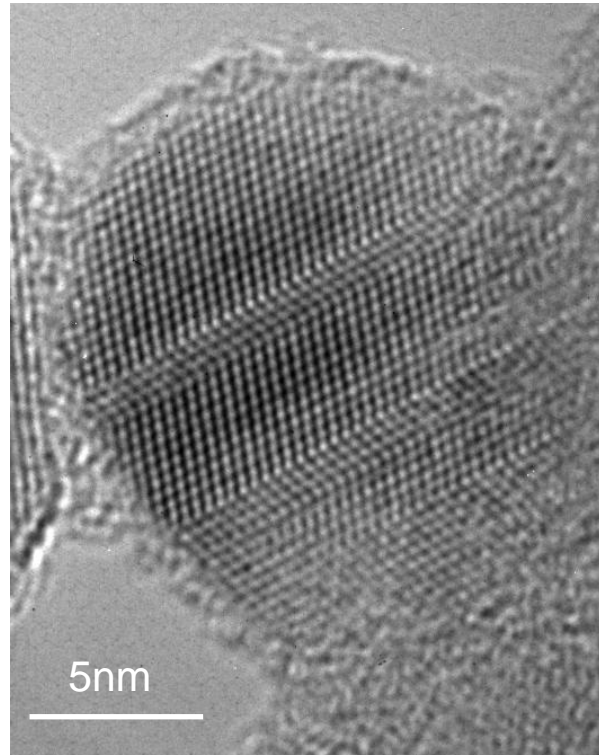


## Different Ar flow rate

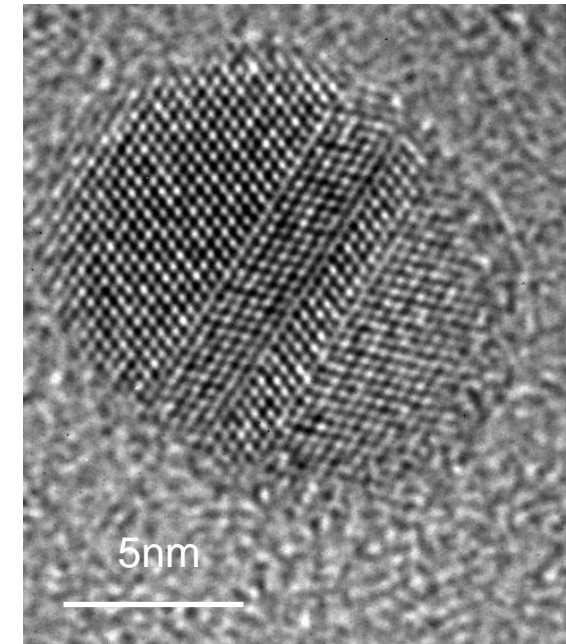
SiH<sub>4</sub> 1 sccm H<sub>2</sub> 1 sccm



Ar 30 sccm



Ar 45 sccm

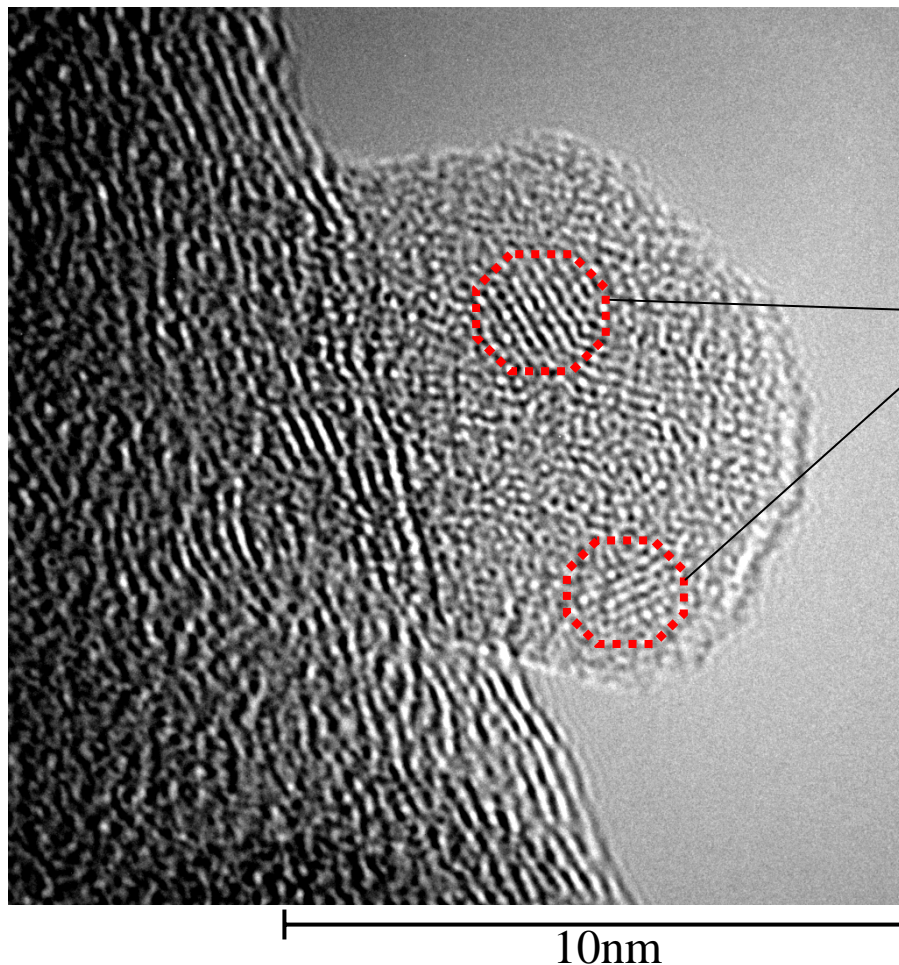


Ar 90 sccm

→ Change of Crystallinity is related to addition of H<sub>2</sub>

## Addition of $H_2$ to background Ar plasma

———— Pulsed  $SiH_4$  in Ar/ $H_2$  plasma



Multi-domain structure

Crystallization is likely to be blocked by adding  $H_2$

# Discussion

## Effects of H<sub>2</sub> dilution

In Si thin film growth by PECVD using H<sub>2</sub>/SiH<sub>4</sub>

H<sub>2</sub> dilution induces change from amorphous to crystalline

N. Shibata *et al.*, Mat. Res. Soc. Symp. Proc. **95**, 225 (1987).

Production of Si nano-particle using VHF discharges

High H<sub>2</sub>/SiH<sub>4</sub> ratio causes better crystallinity

M. Shiratani *et al.*, Trans. Mat. Res. Soc. Jpn. **30**, 307 (2005).

Our results has opposite tendency

Effects of H<sub>2</sub> addition are different in our condition  
using SiH<sub>4</sub>/Ar/H<sub>2</sub> chemistry?



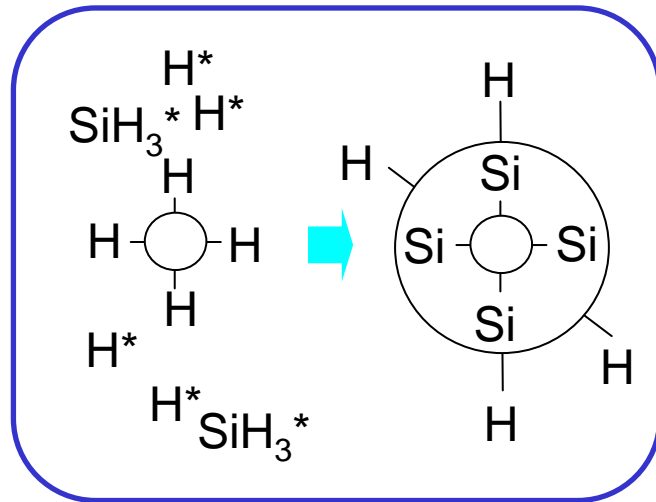
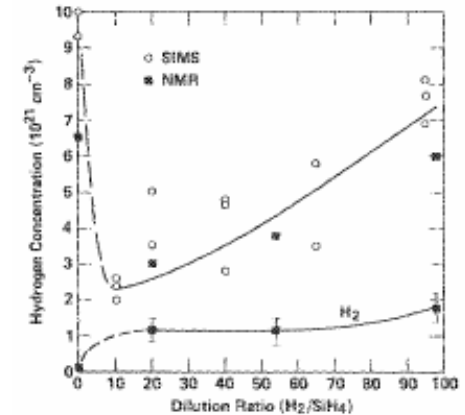
In microcrystalline Si deposition

$H_2$  is incorporated at highly diluted condition

N. M. Johnson *et al.*, Appl. Phys. Lett. **53**, 1626 (1988).

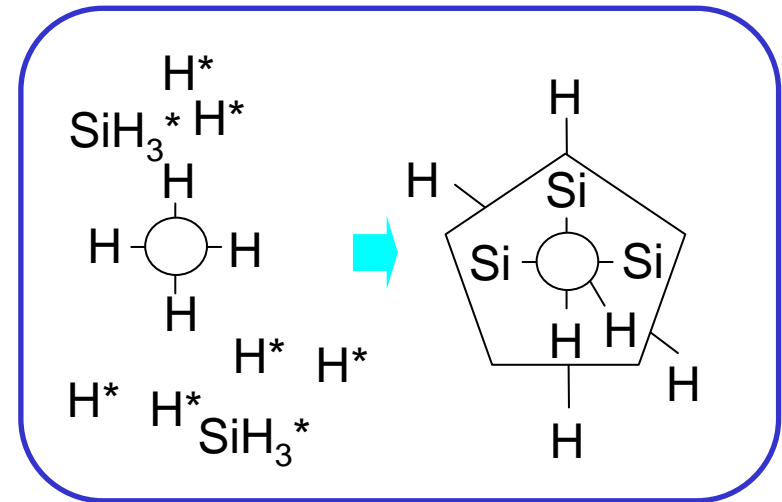
High SND growth rate in Ar plasma

→ Excess  $H_2$  easily incorporated



Sufficient  $H_2$  for crystallization

$H_2$   
added



Amorphous phase

## Why does it happen?

High deposition rate in pulsed  $\text{SiH}_4$  supply to Ar plasma

→ Due to matching effect between ionization energy of  $\text{SiH}_4$  and Metastable state in Ar

Current condition w/o  $\text{H}_2$  actually realized high deposition rate with good crystallinity

→ Might has a tendency to change drastically by slight change of parameter

Quantitative analysis of  $\text{H}_2$  incorporation is important.

## Are SNDs miniaturized?

Actually size of individual SNDs was reduced.  
Preventing aggregation is future issue.

# Summary

We studied SND formation in the pulsed-gas VHF plasma process combined with three gas sources of  $\text{SiH}_4$ , Ar, and  $\text{H}_2$ .

We found that the crystallinity of individual dots changed drastically by adding  $\text{H}_2$  into  $\text{SiH}_4$ /Ar system

Observed effects of  $\text{H}_2$  addition has opposite tendency compared with previous reports, and might be explained as a unique features in our  $\text{SiH}_4$ /Ar/ $\text{H}_2$  system.

Size reduction of individual SNDs by adding  $\text{H}_2$  is useful for future SND applications.