Effect of Si Surface on Cu Nucleation in Aqueous Solutions

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Background and Purpose

- As the device sizes shrink, the tolerance for metal contamination levels on Si surfaces become smaller.
- What is the effect of the surface preparation and chemical state on the metal deposition?
- By understanding the relationship between the Si surface and metal deposition, we hope to find methods to suppress metal deposition and to reduce chemical consumption.

Experimental Methods

- Preparation of H-Si(111)
  - H_2SO_4:H_2O_2 = 4:1 (10min, @ 90°C)
  - DIW rinse
  - Ar-sparged 40% NH_4F (15min, @RT)
- Cu contamination
  - Cu-spiked DI water
    - deposition time
    - Cu^{2+} conc. in DI water
    - misorientation angle
- Preparation of H-Si(100)
  - 1% HF (2min, @RT)
  - DIW rinse
  - H_2SO_4:H_2O_2 = 4:1 (4min, @ 90°C)
  - DIW rinse
  - 1% HF (2min, @RT)
  - (Methanol/I_2 treatment)
- Cu contamination
  - Cu-spiked DI water
    - Cu^{2+} conc. in DI water
    - surface preparation time

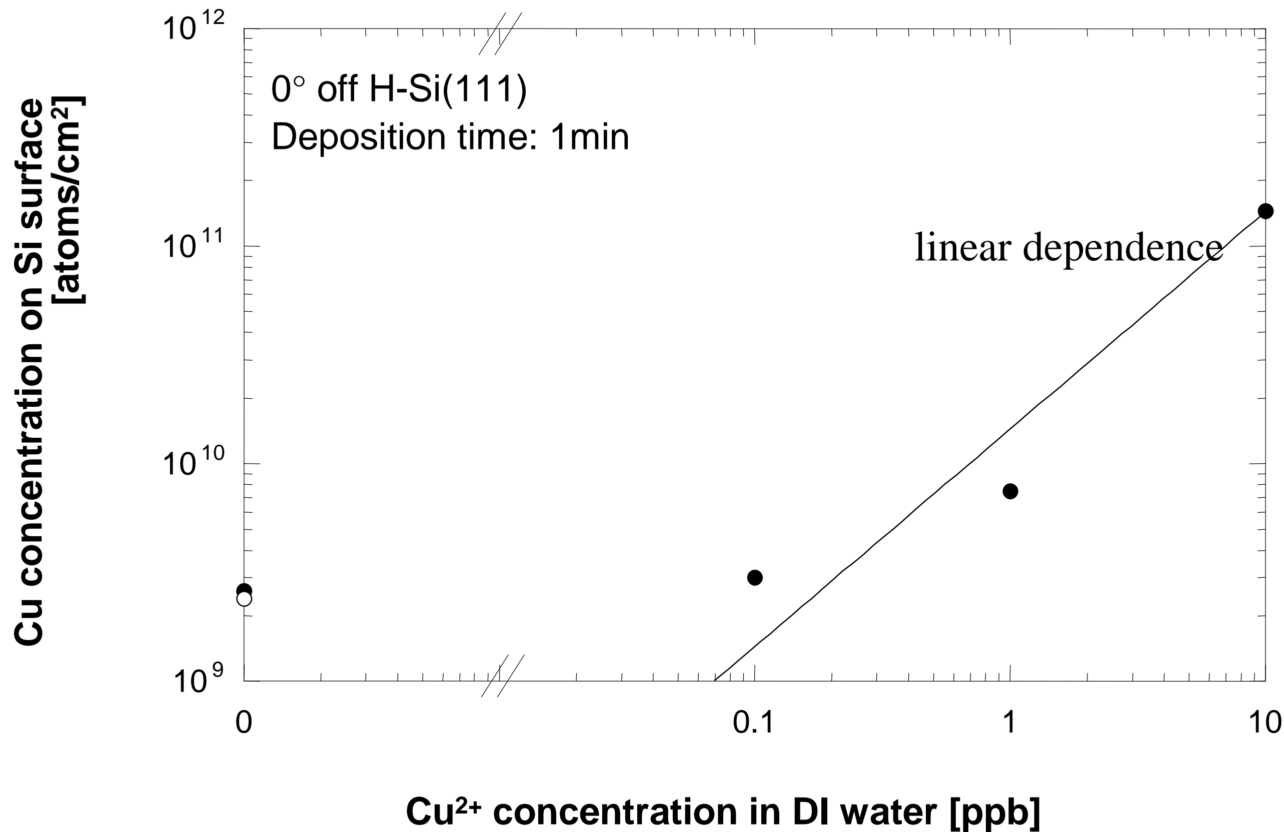
Analysis

- Synchrotron Radiation TXRF
  - Measurement of Cu coverage
    (detection limit: 1×10^{8} atoms/cm^{2})

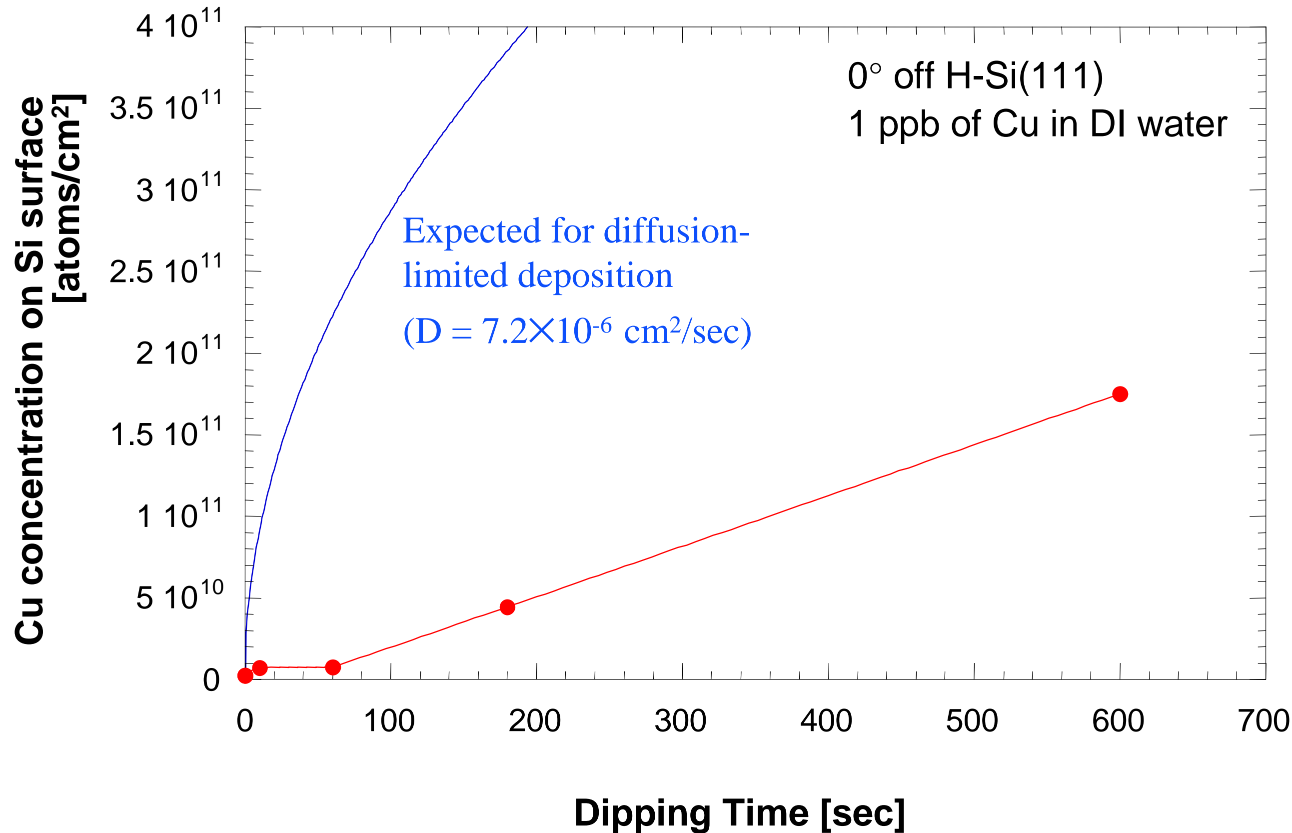
- ATR FT-IR
  - Hydrogen termination & microroughness

- SEM and STM
  - Surface imaging of Cu nucleation and Si surface

Cu Deposition on H-Si(111): Cu^{2+} Conc.



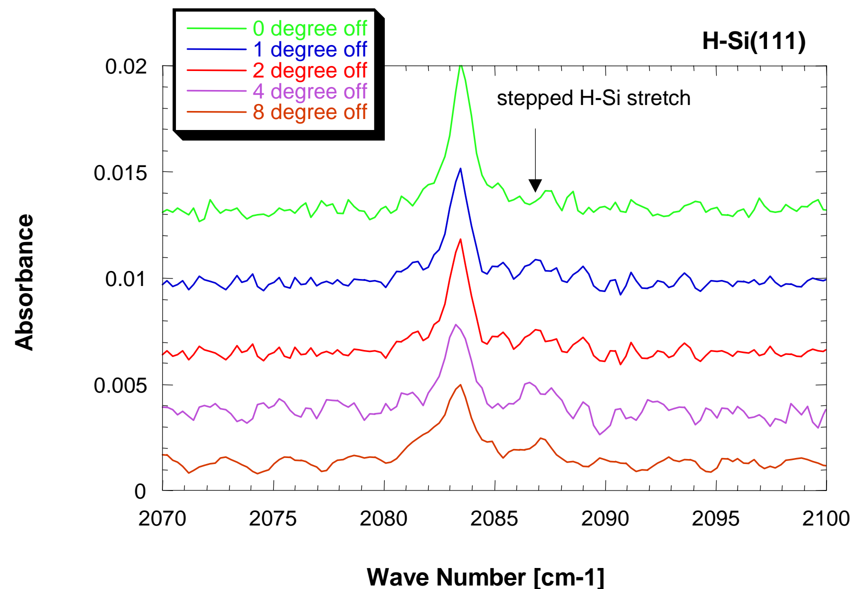
Cu Deposition on H-Si(111): Depo. Time

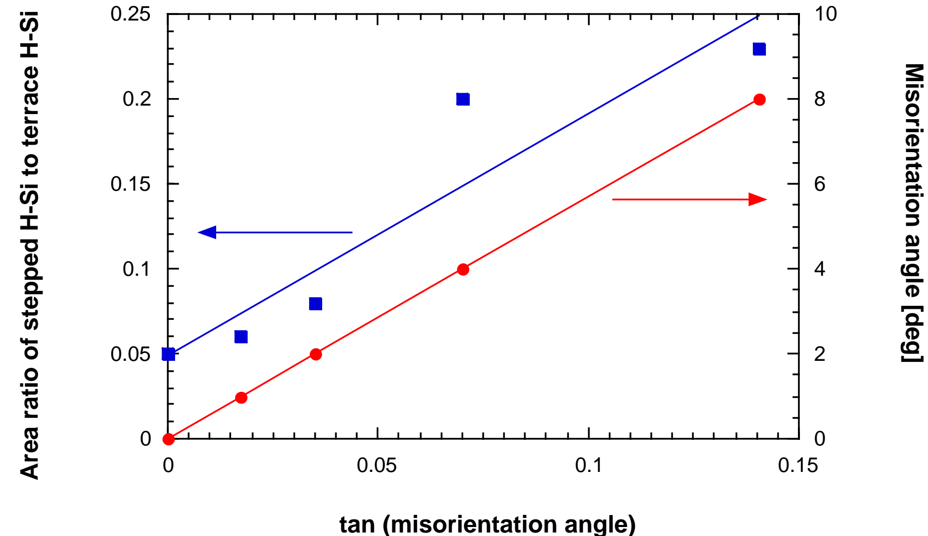


The rate limiting step for electrochemical Cu deposition is surface reaction, not diffusion of Cu^{2+} to the surface.

FT-IR Spectra of H-Si(111)

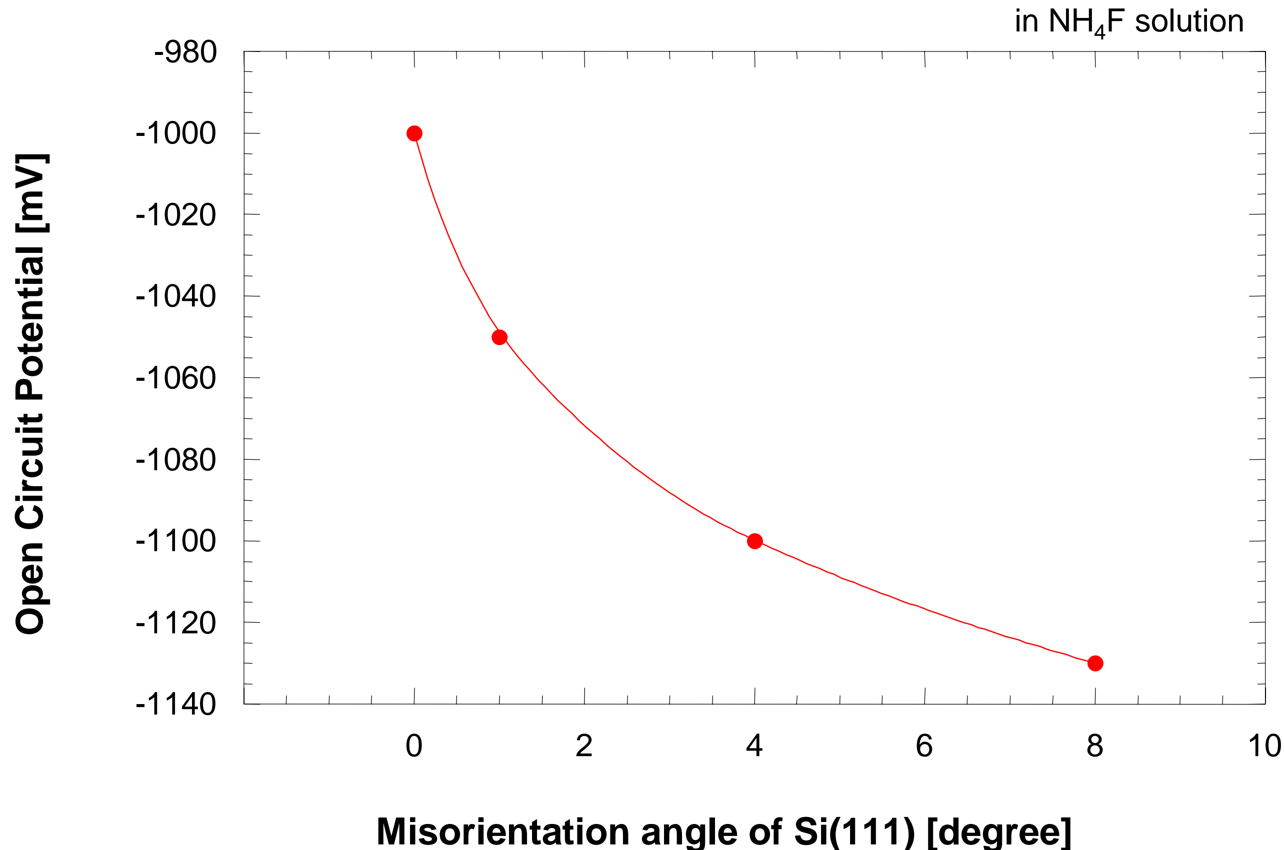
Brewster angle p-polarized transmission FT-IR





Highly misoriented H-Si(111) surface has more stepped H-Si which is linearly proportional to the misorientation angle up to 8°.

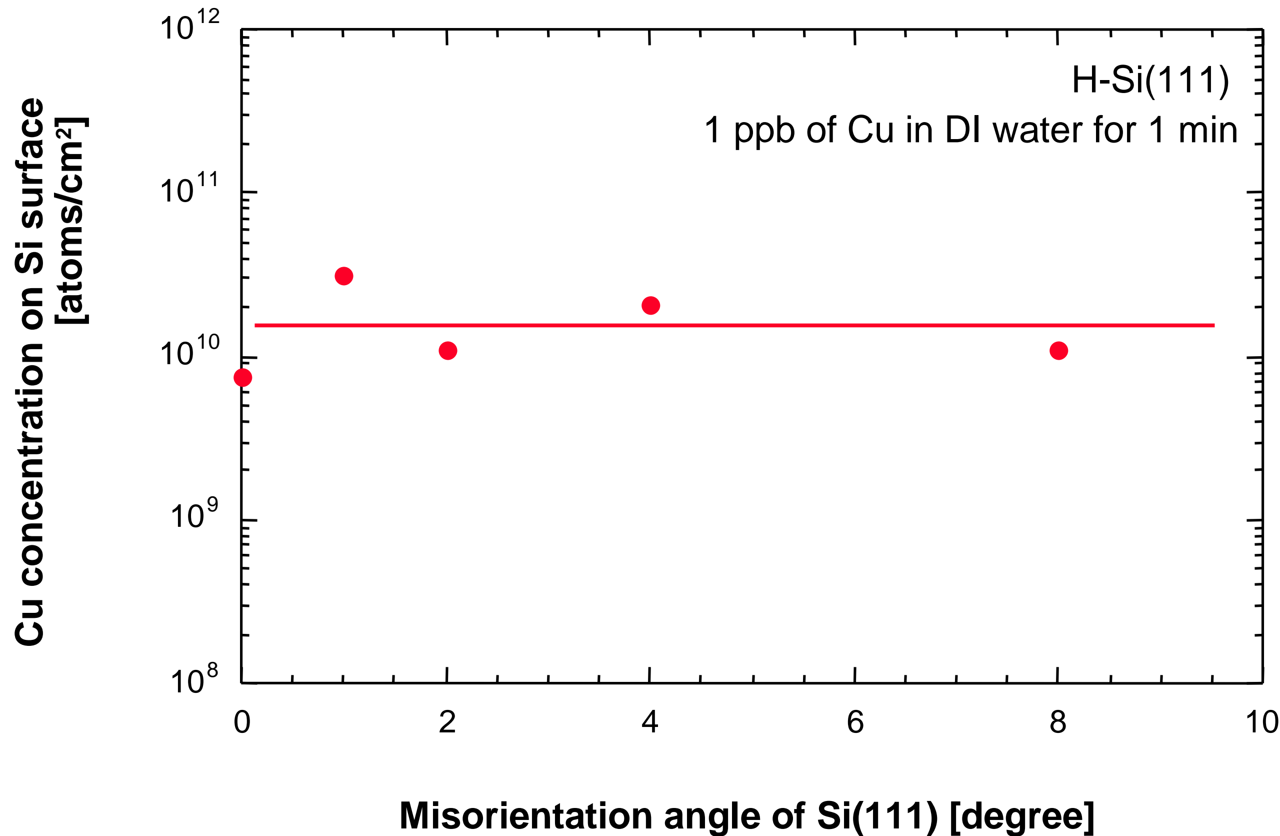
Open Circuit Potential



More misoriented Si(111) surface: more negative OCP

more driving force for Cu^{2+} reduction

Cu Nucleation and Step Density

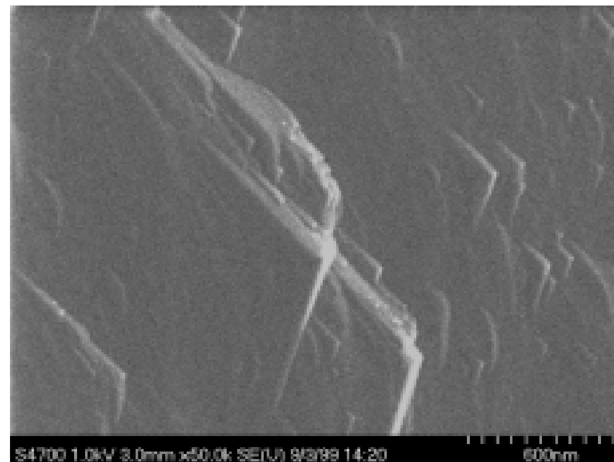


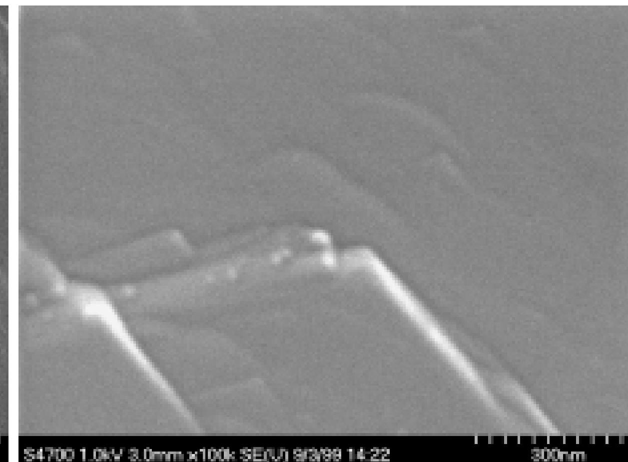
Change of step density on H-Si(111) didn't affect the deposited Cu amount.

SEM Images of Cu Nuclei

2° off

8° off

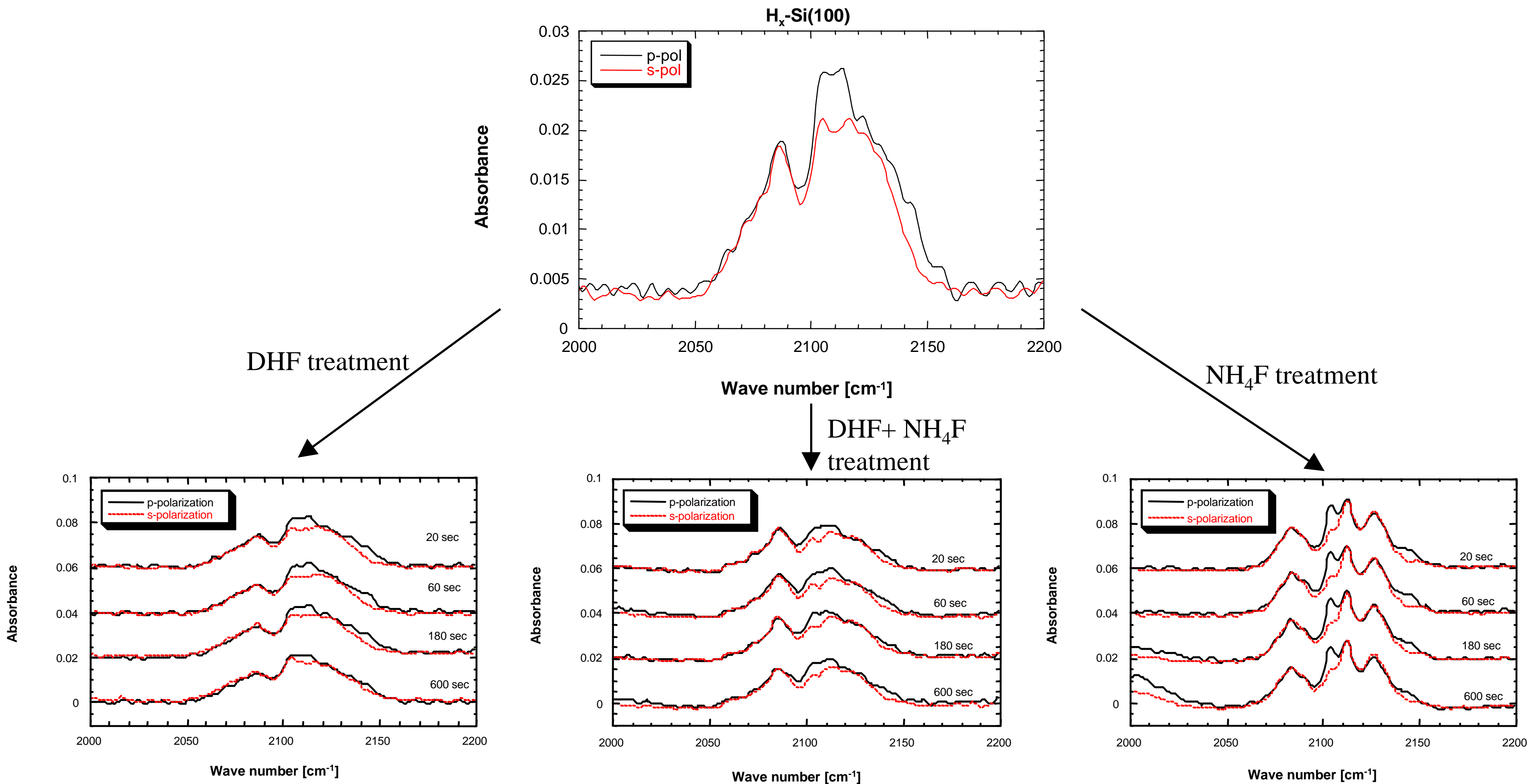




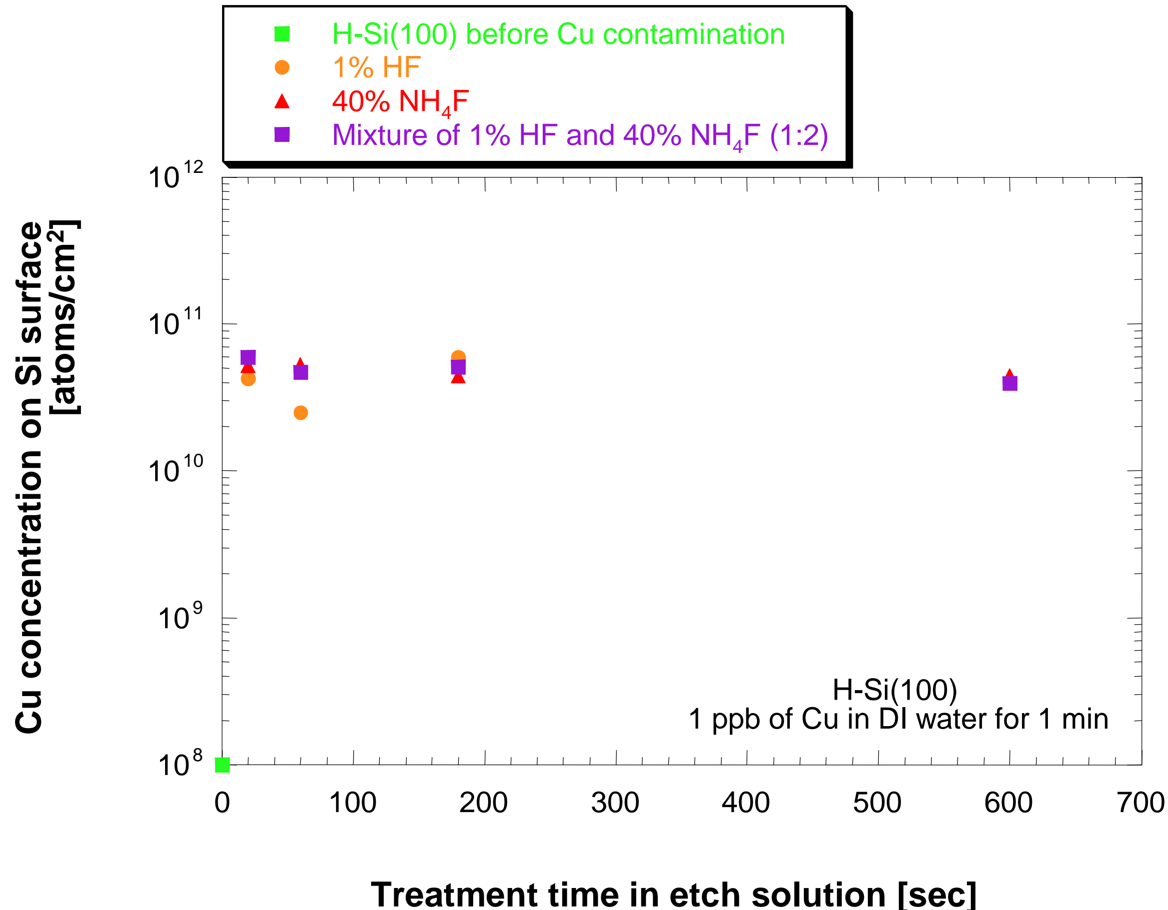
Cu^{2+}: 200 ppb in DI water
Deposition time: 10 min

- Cu nucleation seems to occur on the step edges preferentially.
- The number of nucleus is increased on highly misoriented H-Si(111).
- The size of nuclei on 2° off H-Si(111) is somewhat bigger than those on 8° off.

ATR FT-IR Spectra of H_x-Si(100)

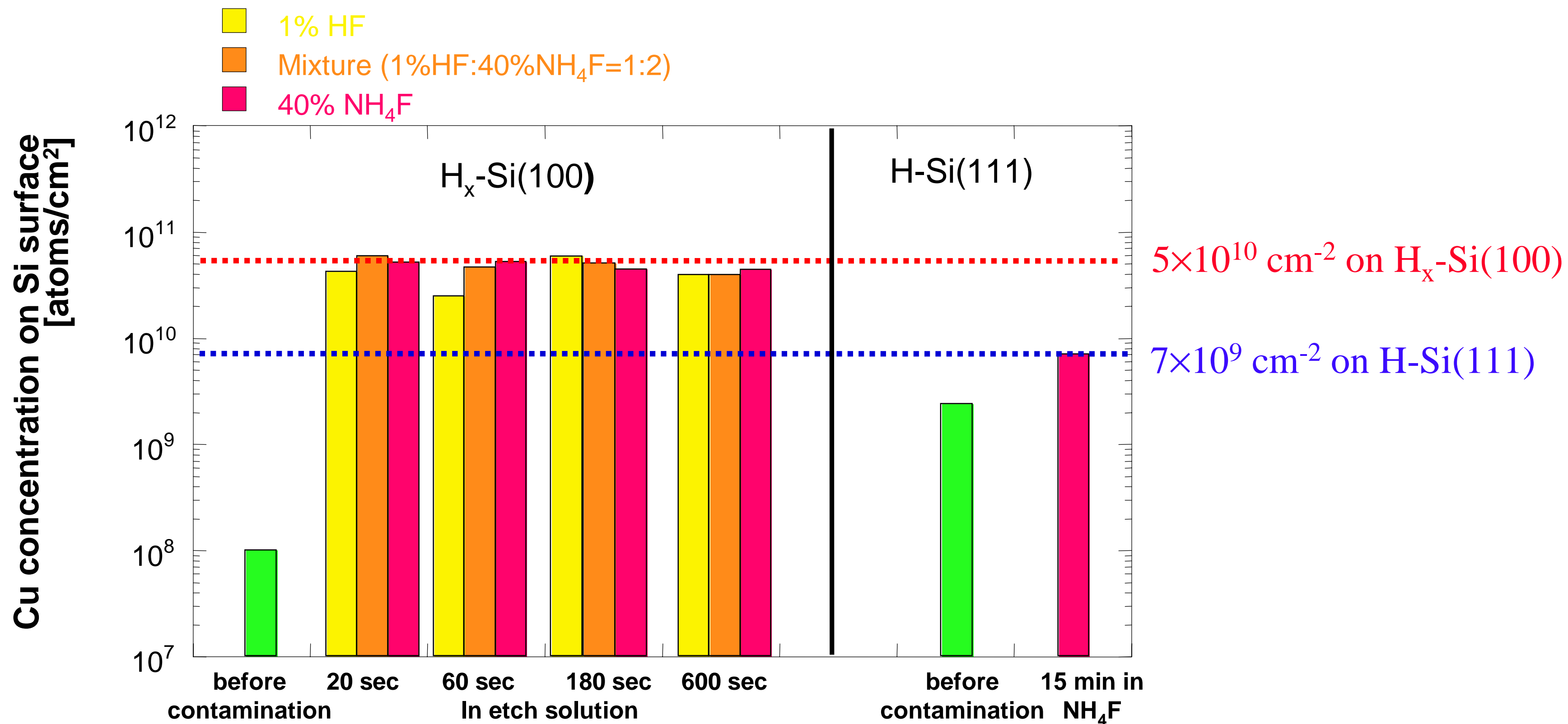


Cu Concentration on H_x-Si(100)



There is no dependence of Cu amount upon the H_x-Si(100) surface modification.

Cu Conc. on H_x-Si(100) &H-Si(111)

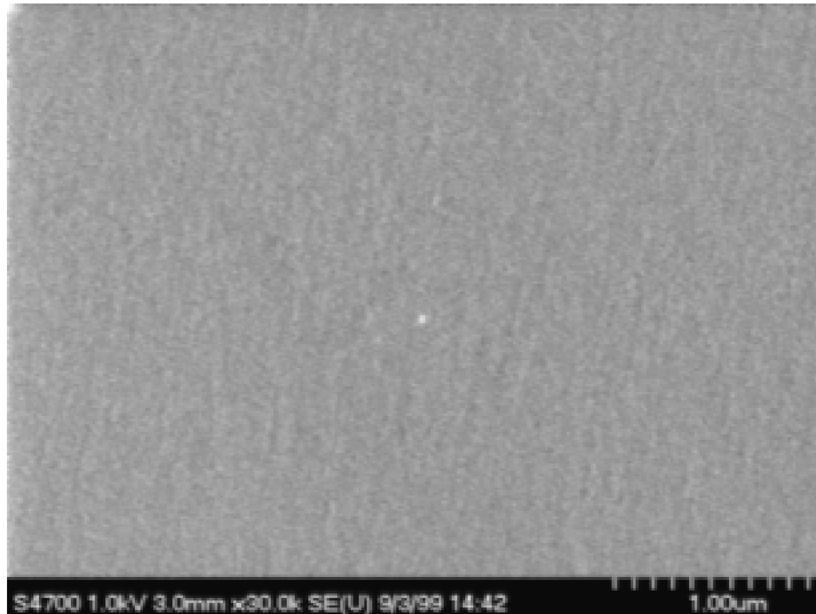


Cu nucleation on H-Si(111) is much less reactive than that on H_x-Si(100).

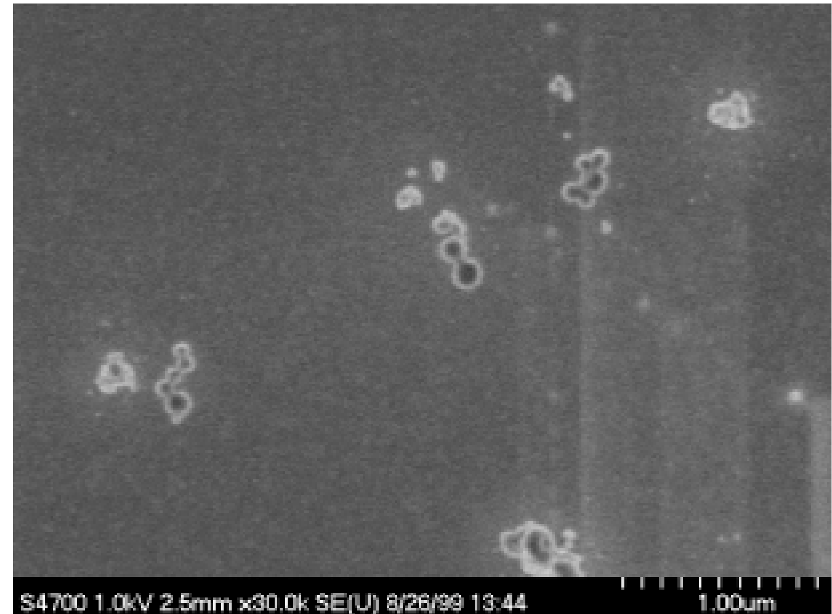
Possible reason: the small number of kink site or dihydride groups on H-Si(111).

Cu Nucleation on H_x-Si(100)

2° H-Si(111)



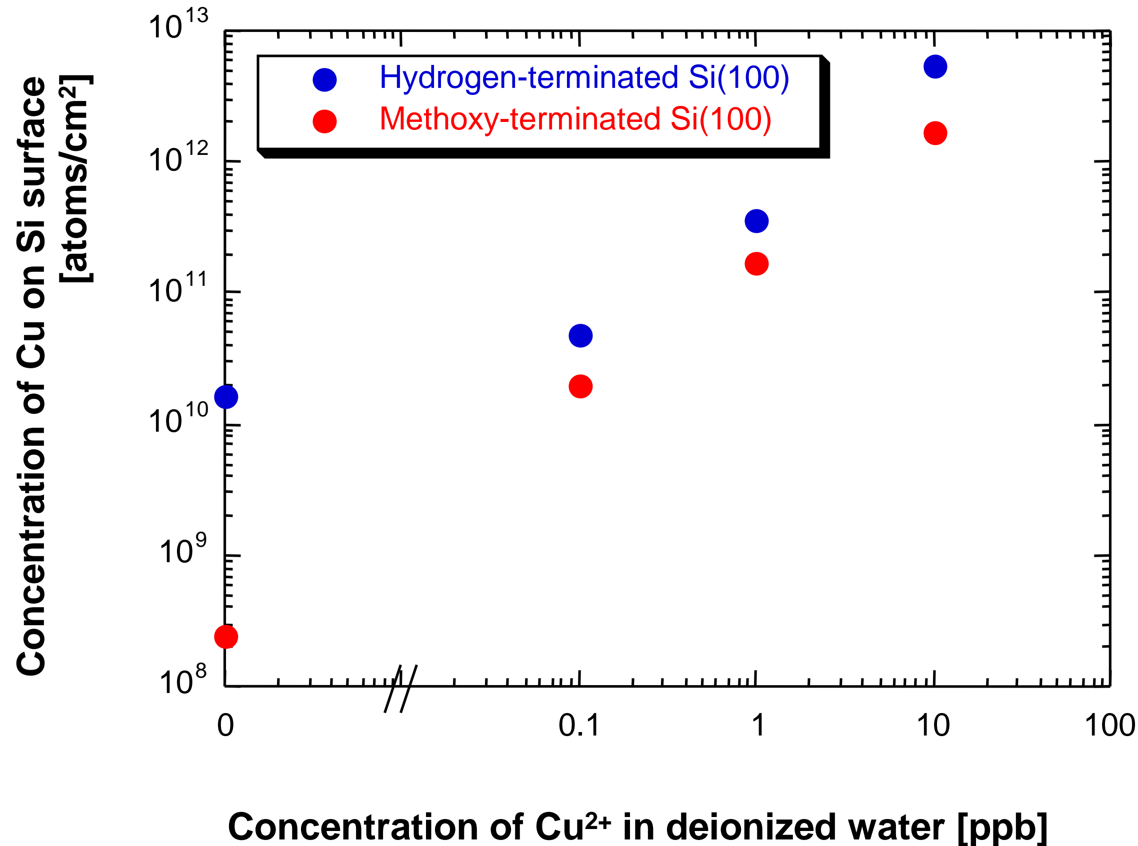
H_x-Si(100)



Cu^{2+}: 200 ppb in DI water
Deposition time: 10 min

Cu nucleation on H_x-Si(100) is very fast and occurs at all surfaces, This may be because the Si(100) surface has many kink sites at which Cu^{2+} can be reduced to metallic Cu.

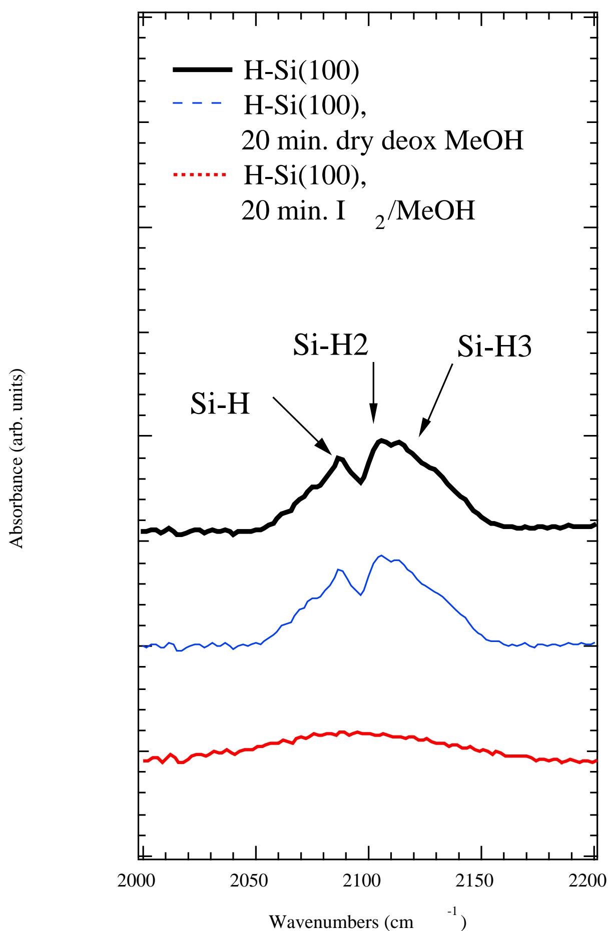
Cu Conc. on H- and MeOH-Si(100)



Methoxy terminated Si(100) : higher resistance to Cu contamination

Possible reason: unreactive methoxy termination of former dihydride sites.

ATR FT-IR Spectra



- H_x-Si(100) is stable in methanol.
- I_2/methanol eliminates H-termination.

Summary

- Cu deposition on H_x-Si(100) in DI water was faster by one order of magnitude than that on H-Si(111). We suggest that the small number of kink sites or dihydride groups is the reason for the lower Cu concentration on H-Si(111).
- Methoxy terminated Si(100) surface showed higher resistance to Cu contamination than H-Si(100). The lower reactivity of methoxy terminated sites may be the reason.
- Contrary to our expectation, the change of step density (1° to 8° off) on H-Si(111) didn't affect the amount of deposited Cu. We suggest that this is because the change in kink site density is small compared to that between Si(100) and Si(111).
- One method to suppress the Cu contamination on Si surface may be to control the number and reactivity of dihydride sites on the surface.