

# Effect of H<sub>2</sub> adding and substrate bias to Cu sputtering

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## 1. Introduction

Recently, Cu is widely used in ULSI for metal interconnection. The merits of Cu are (1) resistivity of Cu (1.7  $\mu\Omega\text{cm}$ ) is lower than that of Al or Al alloys and (2) higher resistance to electromigration [1-4]. There are many deposition techniques for Cu film on Si wafer. The popular techniques for filling trenches or vias are metal organic chemical vapor deposition, electroplating and electroless plating. Today, Cu electroplating is most popular technique. A conformal and conductive seed layers is necessary for Cu electroplating. The seed layer is generally deposited by sputtering.

Yokoyama *et al.* reported that the crystallinity of single-crystal Al(110) film grown on a vicinal Si(100) substrate has been improved by adding a small amount of hydrogen (0.5%) into the sputtering gas (Ar) and applying a positive substrate bias voltage [5]. The hydrogen effect may be attributed to the migration enhancement by hydrogen-termination of the Al surface. Oh *et al.* reported the effects of plasma H<sub>2</sub> pretreatment and also the combined effects of plasma H<sub>2</sub> pretreatment and rapid thermal annealing of the Cu seed layers[6]. The plasma H<sub>2</sub> treatment can remove carbon and oxygen contaminants from the Cu seed layer giving more Cu atoms free for electroplating. We think that H<sub>2</sub> adding is effective for coverage to sub-micron hole in metal sputtering.

In this paper, we study the effect of H<sub>2</sub> adding and substrate bias to Cu sputtering.

## 2. Experiments

DC magnetron sputtering system we used is schematically shown in Fig. 1. The source DC voltage is set to 500 V. The various voltage is applied to the substrate. Pressure is 5 mTorr. Plasma source gas is Ar or mixture of Ar and H<sub>2</sub> (20%).

The schematic sample structure is shown in Figs. 2 and 3. A 900 nm thick phosphosilicate-glass (PSG) layer is deposited on the Si wafers and the several size of holes are formed on it. Then a TiN film is sputtered with the thickness of 30 nm as a diffusion barrier or/and adhesion promoter.

## 3. Results and Discussions

### 3.1 Effect of bias voltage

The effect of bias voltage was investigated. The bias voltage was varied from 0 V to -100 V. And Ar plasma used. The cross sectional SEM photograph of the sputtered Cu in 0.4  $\mu\text{m}$  square hole is shown in Fig. 4. The Cu thin film (30 nm) is deposited only on the side wall and not at the bottom of the hole. And the effect of bias voltage to coverage of Cu is not observed on the surface of the hole. The morphology of the Cu film

sputtered to the 0.1  $\mu\text{m}$   $\phi$  hole is shown in Fig. 5. However, Cu film is not deposited inside the 0.1  $\mu\text{m}$  hole. We expected that Cu atoms reach the bottom of the high aspect hole by bias voltage. But according to Figs. 4 and 5, Cu atoms cannot be deposited on the bottom of the high aspect hole.

### 3.2 Effect of bias voltage with H<sub>2</sub> adding

Next, the effect of H<sub>2</sub> adding was investigated. The plasma source gas is changed to the mixture of H<sub>2</sub> (20%) and Ar from the pure Ar. And the bias voltage is varied from +10 V to -300 V. The Cu film sputtered to 2  $\mu\text{m}$  square hole is shown in Fig. 6. As compared with sputtering using pure Ar gas, Cu surface on the sidewall is much smoother in case of H<sub>2</sub> adding. In case of H<sub>2</sub> adding, hydrogen-termination occurs on the surface of deposited Cu. And migration of Cu atoms is enhanced (see Fig. 7) which causes the Cu surface flat. It is only the sidewall that this smoothing effect works, because there is no influence of ion bombardment on the sidewall. On the other hand at the top surface the Ar ion bombardment may cause the surface roughness.

## 4. Conclusions

By addition of H<sub>2</sub> to Ar plasma in Cu sputtering, it is found that the sidewall surface becomes flat.

This effect will be useful for obtaining the high quality smooth Cu seed layer.

## 5. Acknowledgement

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## References

- [1] J. Musil *et al.*: *Czech. J. Phys.* **45** (1995) 249.
- [2] J. C. Chiou *et al.*: *J. Electrochem. Soc.* **142** (1995) 177.
- [3] V. M. Donnelly *et al.*: *J. Vac. Sci & Technol. A* **11** (1993) 66.
- [4] V. Dubin *et al.*: *Electrochem. Soc. Proc.* **98-6** (1998).
- [5] S. Yokoyama *et al.*: *Jpn. J. Appl. Phys.* **33** (1994) 459.
- [6] J. Oh *et al.*: *Jpn. J. Appl. Phys.* **40** (2001) 5294.

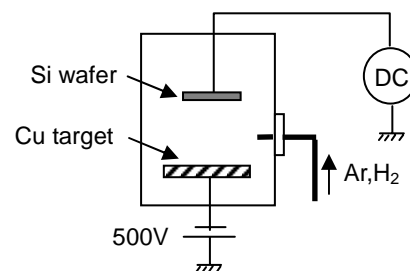


Fig. 1 Schematic diagram of magnetron sputtering apparatus.

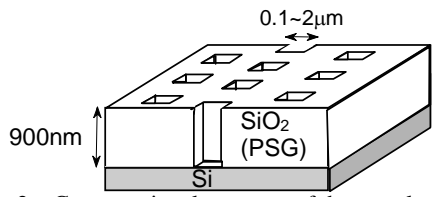


Fig. 2 Cross sectional structure of the sample.

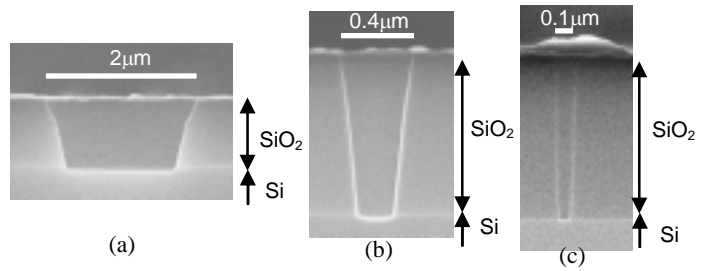


Fig. 3 SEM photographs of cross section of (a) 2 µm square (b) 0.4 µm square and (c) 0.1 µm φ hole before sputtering.

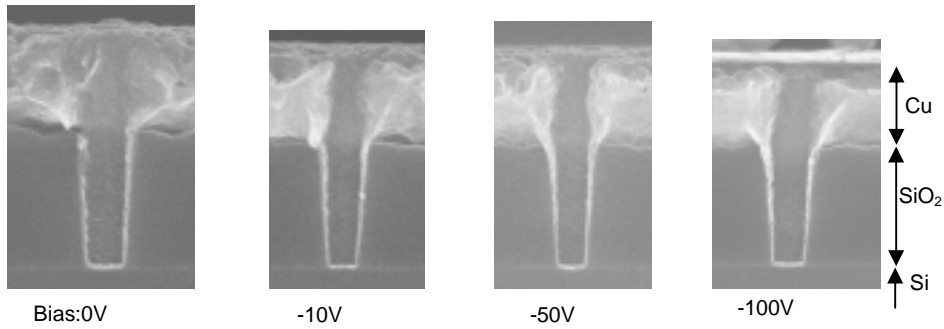


Fig. 4 SEM photographs of cross section of 0.4 µm square hole after sputtering with bias voltage.

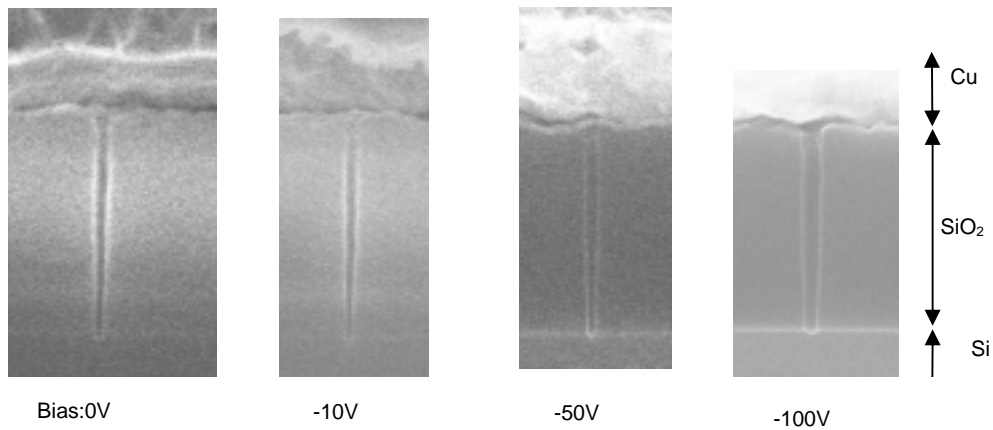


Fig. 5 SEM photographs of cross section of 0.1 µm φ hole after sputtering with bias voltage.

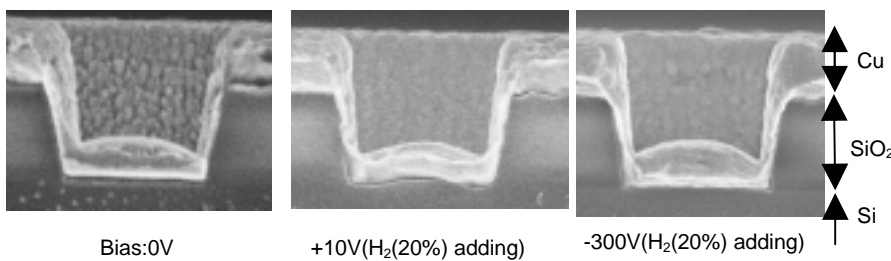


Fig. 6 SEM photographs of cross section of the 2 µm square hole after Cu sputtering.

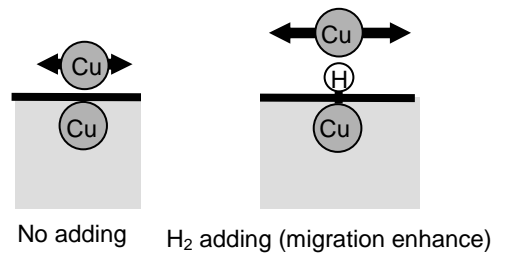


Fig. 7 Mechanism of H<sub>2</sub> adding effect.

# Effect of H<sub>2</sub> adding and substrate bias to Cu sputtering

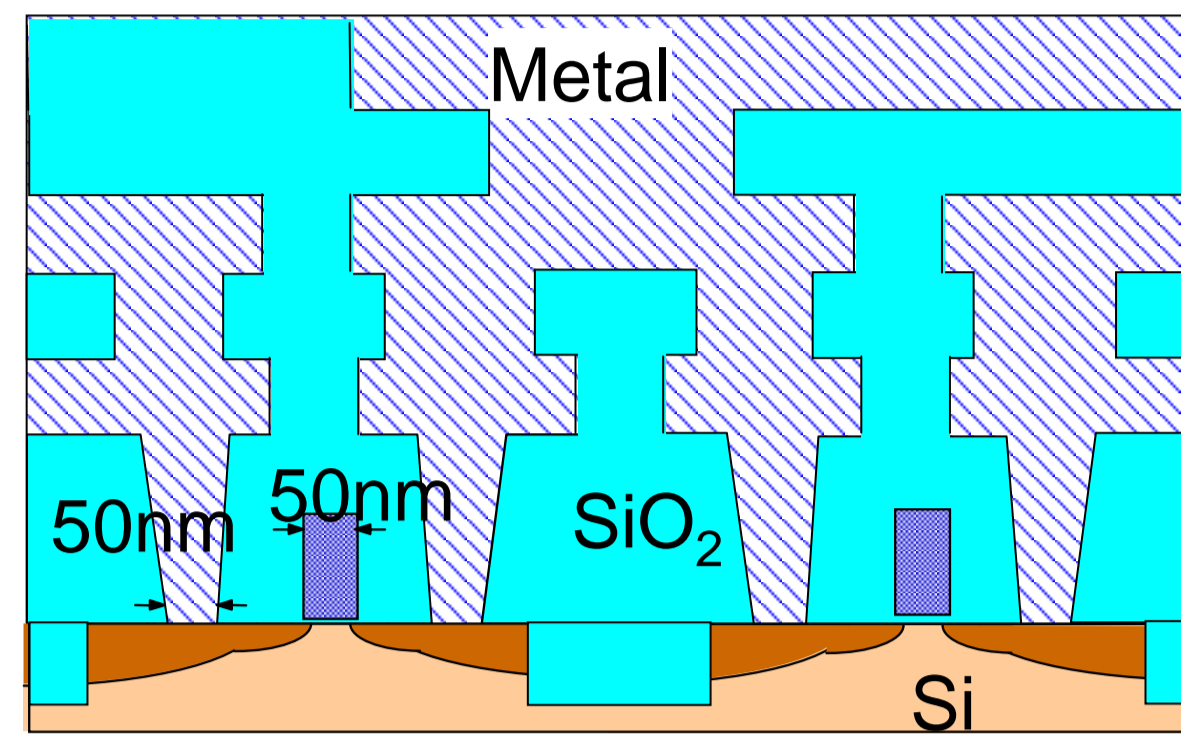
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## Introduction

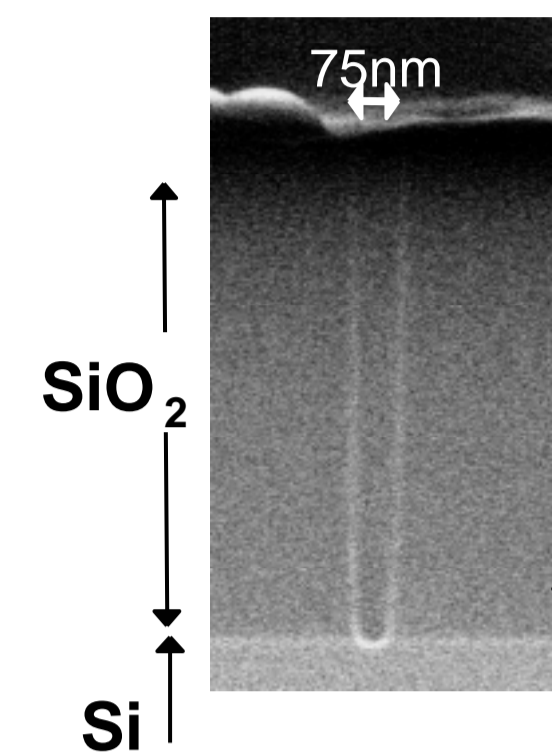
Metal Interconnect Fabricated in ULSI Using Sputtering  
Step coverage of metal filling sub-micron hole or trench pattern is degraded.

Popular techniques for filling trenches or vias  
· Metal organic chemical vapor deposition,  
· Electroplating  
· Electroless plating.  
Influence of metal on organic is assumed.



Contact Hole Formation

- Plasma etching by C<sub>5</sub>F<sub>8</sub>(11sccm)/Ar(60sccm)/NH<sub>3</sub>(2sccm) mixture gas.
- Selectivity (SiO<sub>2</sub>/Si) ≅ 60
- Aspect ratio >10



Contact holes with High Aspect Ratio and High Selectivity is achieved.  
Metal filling is needed.

Sputtering ··· without organic

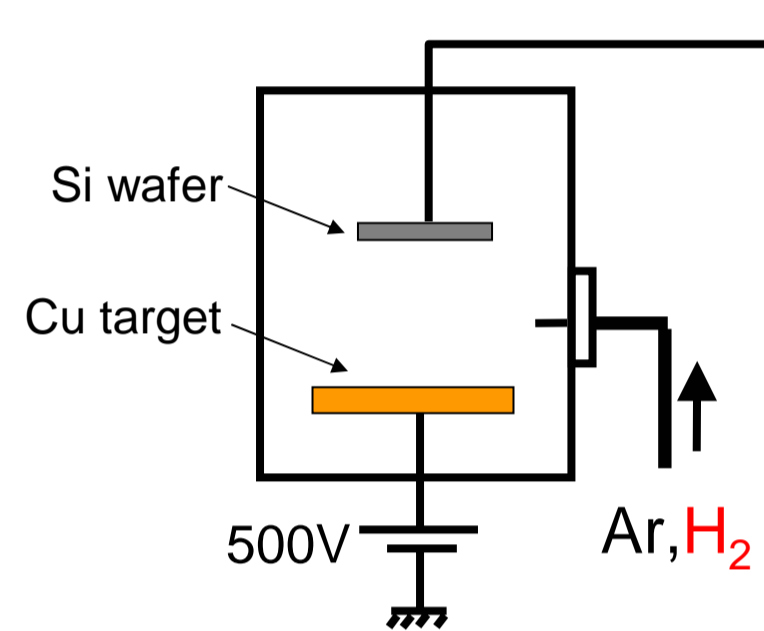
Hydrogen may be affect to the migration enhancement of Cu atoms on surface.

Hydrogen adding is effective to sputtered Al (S. Yokoyama et al. Jpn. J. Appl. Phys. 33 p.459)

We study effect of H<sub>2</sub> adding and substrate bias to Cu sputtering.

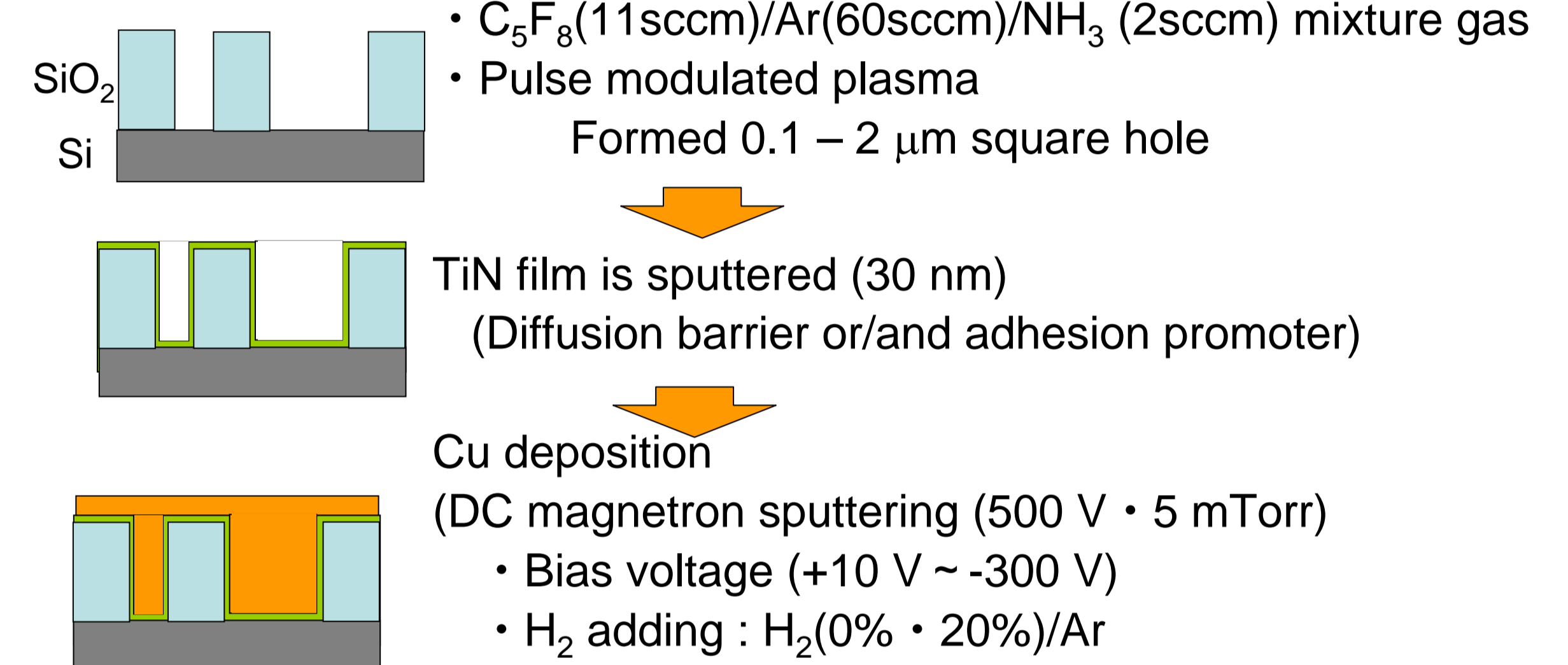
## Experiment

### Magnetron Sputtering Apparatus



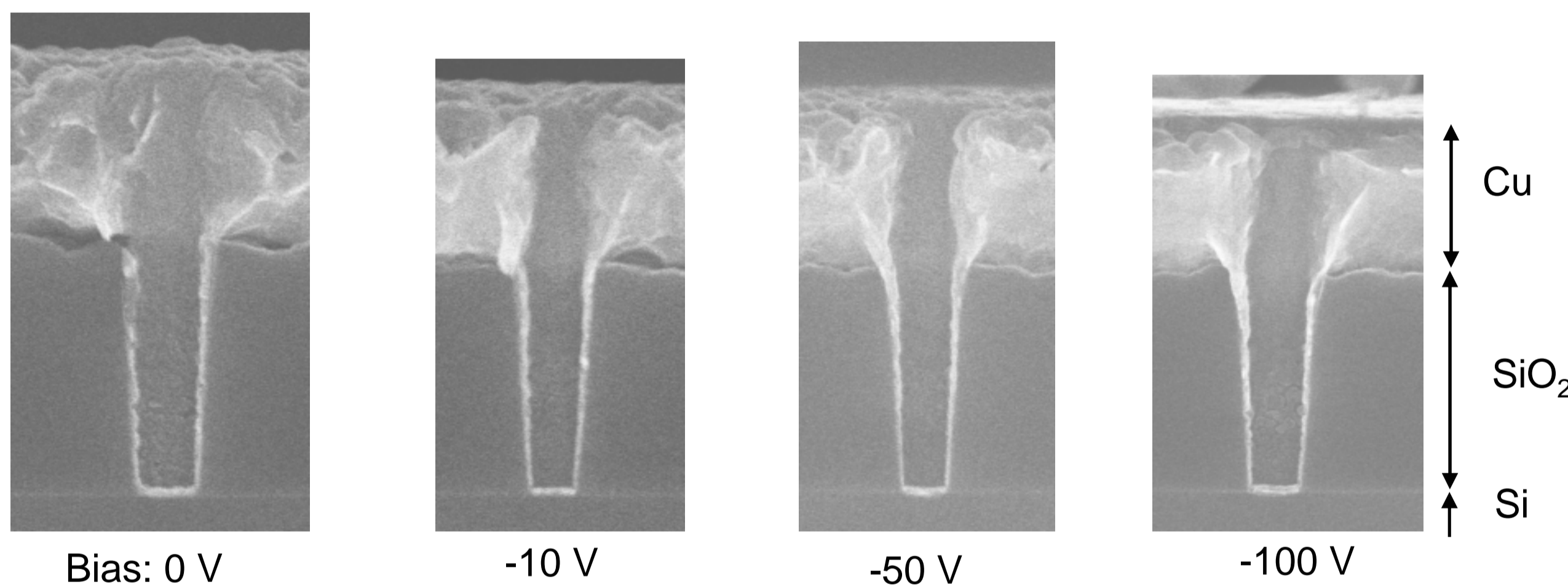
- Effect of bias voltage and H<sub>2</sub> adding is investigated.
- Ion acceleration by bias voltage
- Migration of Cu atoms is enhanced by H<sub>2</sub> adding

### Process Flow



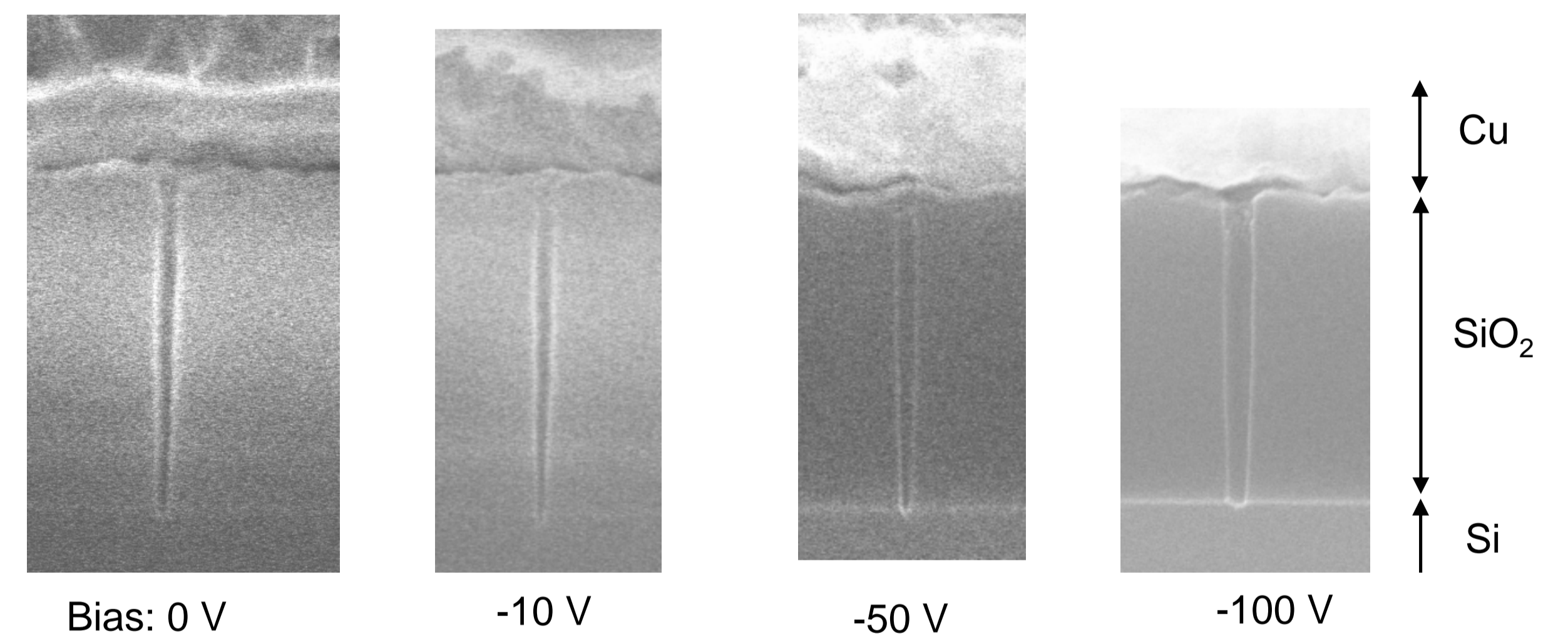
## Effect of Bias Voltage

Large pattern (Holesize:0.4 μm square)



- Cu thin film (30 nm) is deposited only on side wall and not at bottom of the hole.
- Effect of bias voltage to coverage of Cu is not observed on surface of hole.

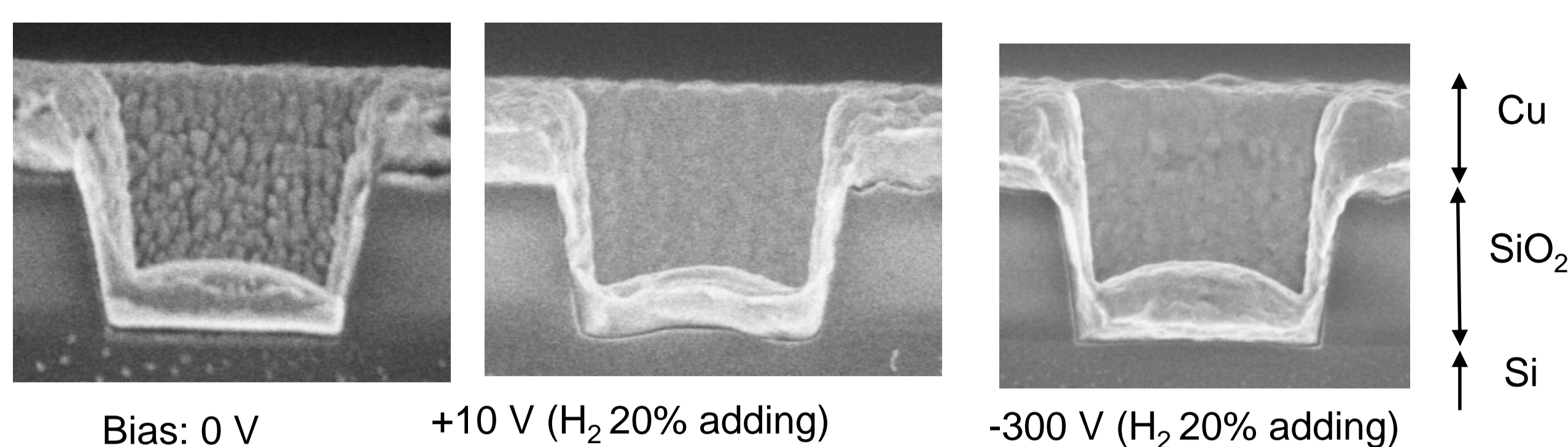
Small pattern (Holesize:0.1 μm )



- Cu film is not deposited inside the hole.

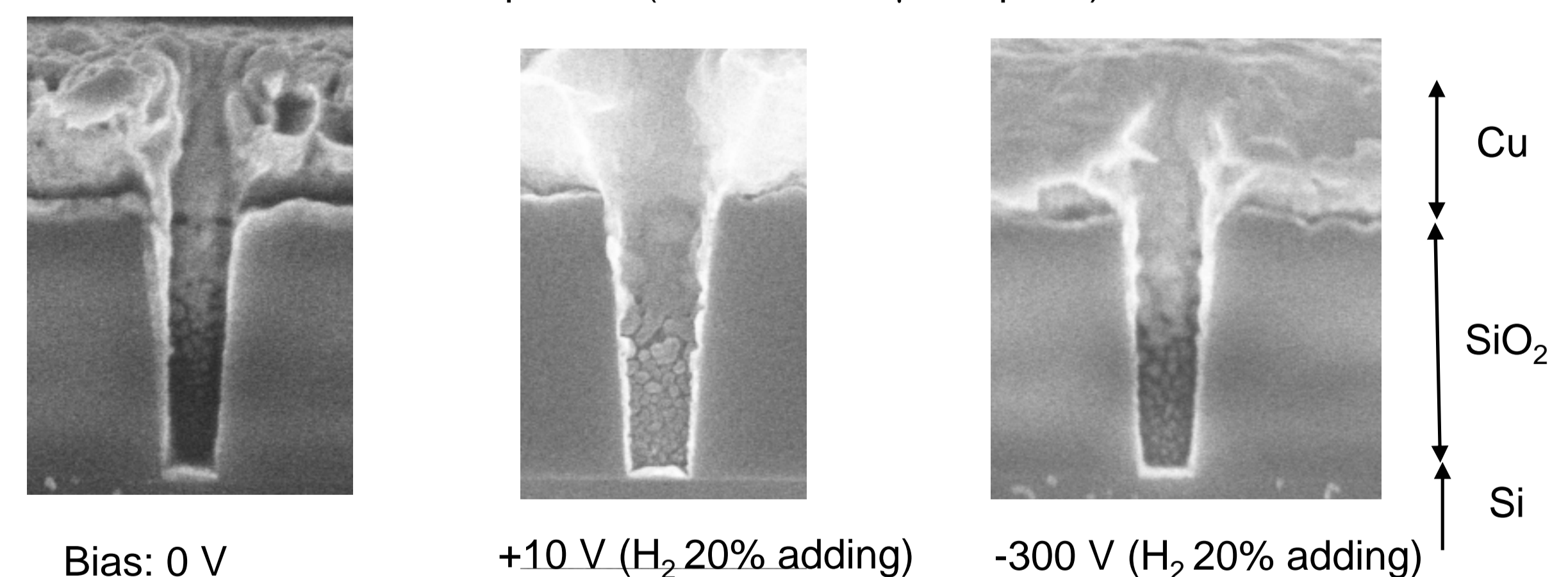
## Effect of H<sub>2</sub> Adding with Bias Voltage

Large pattern (Holesize:2 μm square)



- Cu surface on sidewall is much smoother in case of H<sub>2</sub> adding.
- There is no influence of ion bombardment and the effect of hydrogen radical is shown on the sidewall.

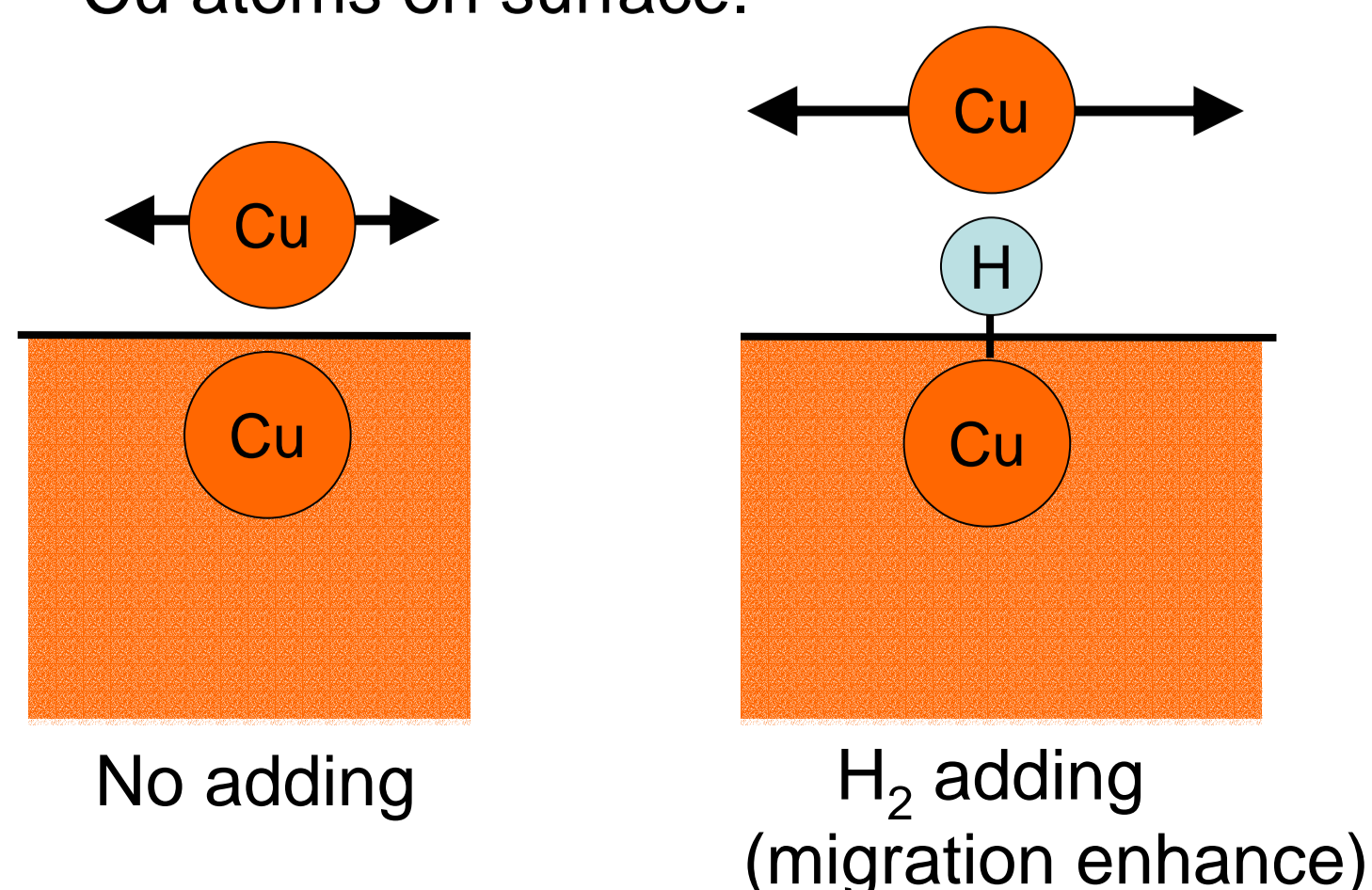
Small pattern (Holesize:0.4 μm square)



- Effect of sidewall reflowing by hydrogen addition was not seen. Since hydrogen radicals move in the various directions, it thinks because penetration of the hydrogen inside the high aspect ratio hole becomes difficult.

## Mechanism of H<sub>2</sub> Adding Effect

Hydrogen-termination enhances migration of Cu atoms on surface.



## Conclusions

Summary

- Bias voltage is not effective to improve filling property of sputtered Cu in sub-micron hole.
- Addition of H<sub>2</sub> to Ar plasma during Cu sputtering Sidewall surface becomes smooth.

Future Work

- Detailed investigation of H<sub>2</sub> and bias effect
- Influence of H<sub>2</sub> adding to electric characteristic of Cu film