

Lithography-Free Fabrication of Transparent Conductive Single-Walled Carbon Nanotube Films

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Single-walled carbon nanotubes (SWNTs) have excellent electrical conductivity, flexibility, and mechanical strength. Consequently, they are a promising candidate material for transparent conductive films (TCFs)^[1]. However, maximal performance of transparency and conductivity is hindered by the trade-off relationship between both characteristics in regard to SWNT film density. One method of improving this balance is patterned growth of SWNT films into low-density regions favorable to transparency and other high-density regions favorable to conductivity, which has proven feasible through previous researches^[2, 3]. However, these previous methods involve lithography or complex treatments that arrange the SWNTs into TCFs after growth. We present a method to fabricate as-grown SWNT TCFs using self-assembled metal masks that is easier and more efficient than methods described in previous studies. The metal masks for selective catalyst deposition are created by annealing thin films of metal to realize an “island” morphology of patterned metal clumps and exposed substrate. This is followed by catalyst deposition and SWNT growth using alcohol catalytic chemical vapor deposition (ACCVd)^[4]. We demonstrate SWNT patterned TCFs with higher transparency and comparable conductivity to continuous thin-films. Furthermore, the efficacy of our SWNT TCFs is demonstrated by utilizing them in CNT-Si solar cells.

[1] Z. Wu *et al.* Science, **305**, 1273 (2004).

[2] N. Fukaya *et al.* ACS Nano, **8**, 3285 (2014).

[3] K. Cui *et al.* J. Phys. Chem. Lett. **4**, 2571 (2013).

[4] S. Maruyama *et al.* Chem. Phys. Lett. **360**, 229 (2002).

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Introduction

Motivation

Desirable properties of single-walled carbon nanotubes (SWNTs):

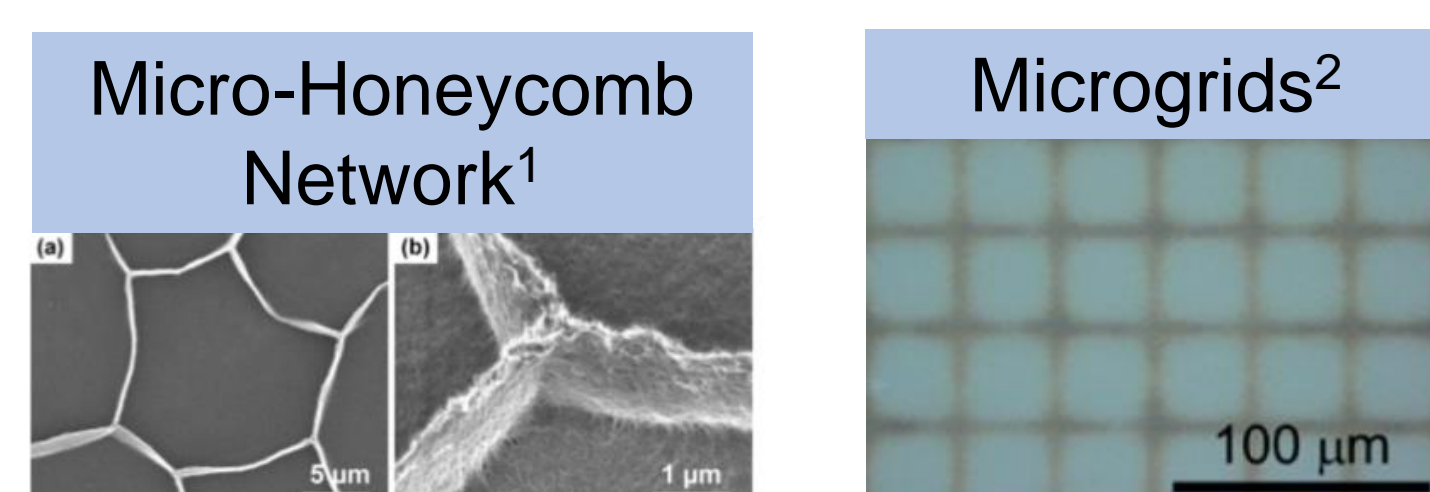
- Flexibility
- Mechanical strength
- Electrical conductivity

SWNTs have potential for use in electronic devices, such as through transparent conductive films (TCFs).

Problem

- Trade-off relationship between transparency and conductivity in regard to SWNT film density

- Can be overcome using patterned SWNT films:



- High density region:
 - Promote conductivity
- Low density region:
 - Increase transparency

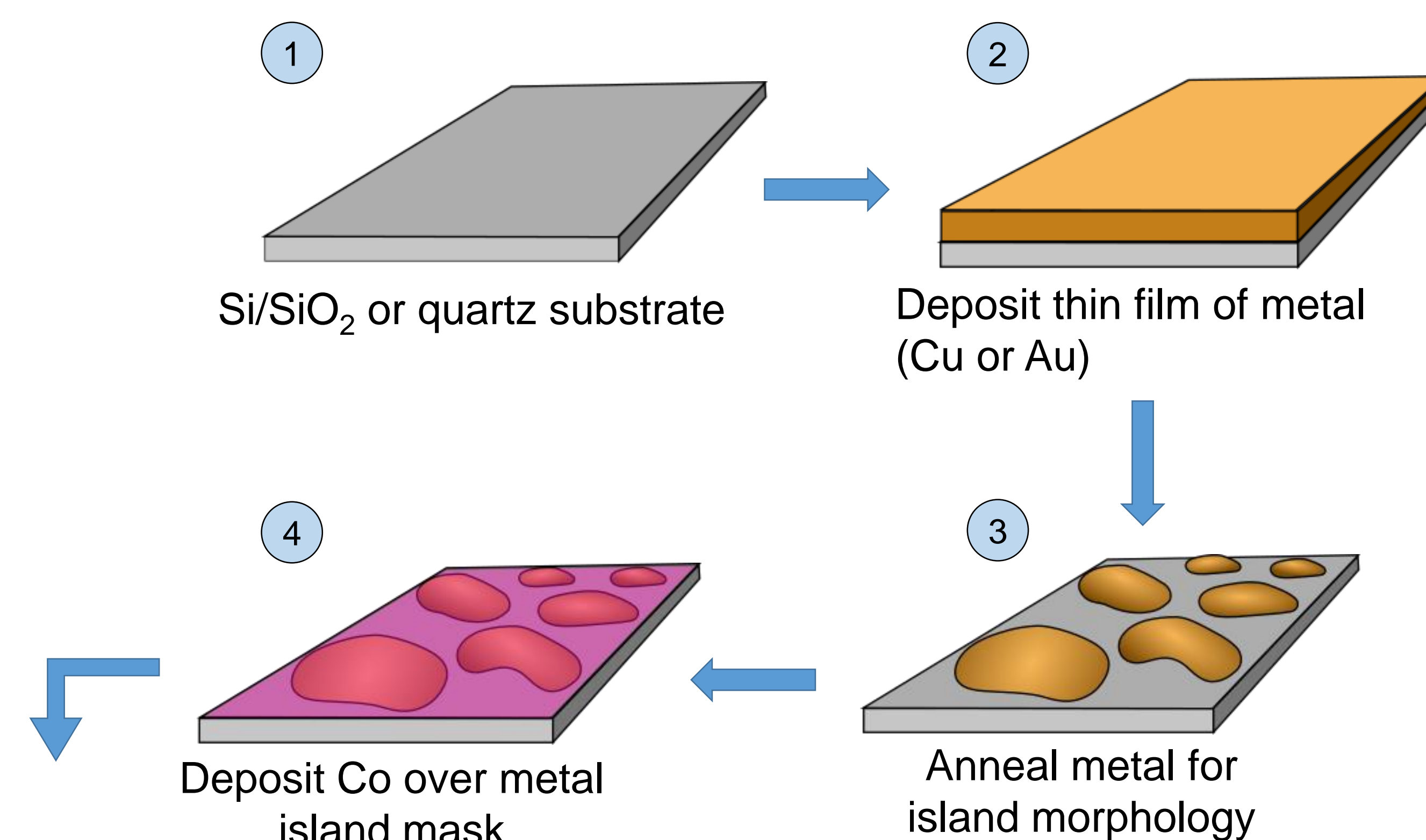
However, current methods involve lithography or complex treatment after growth.

Goal

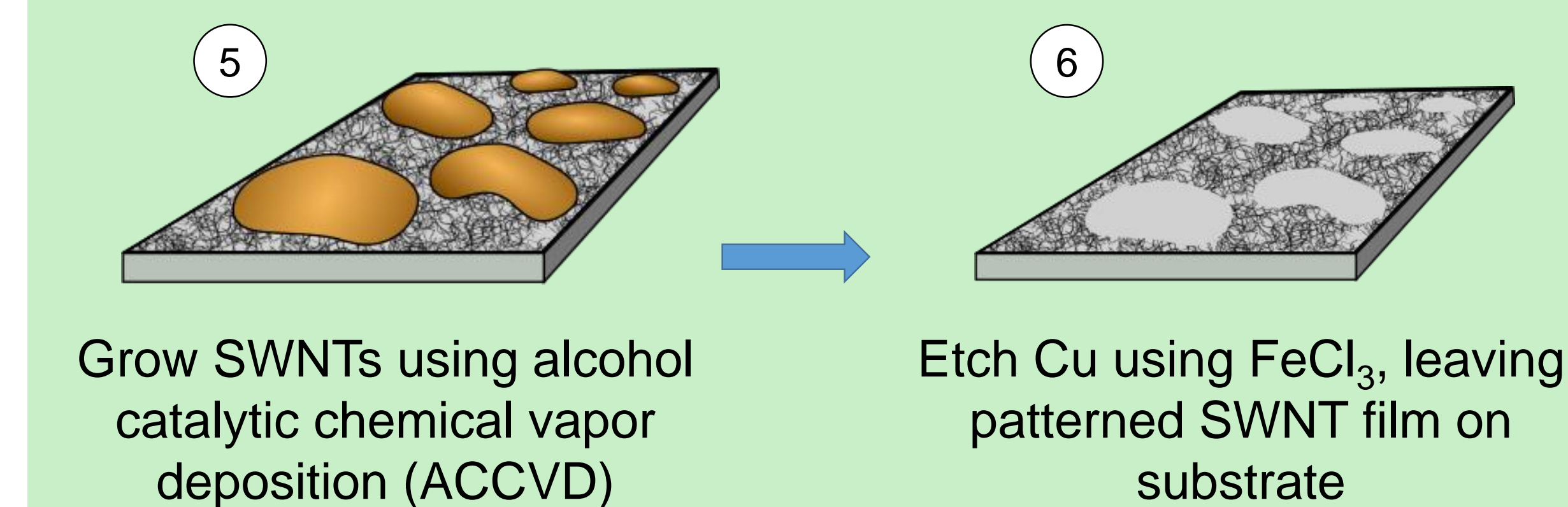
Use self-assembled metal masks for selective catalyst deposition to pattern SWNT growth into TCFs.

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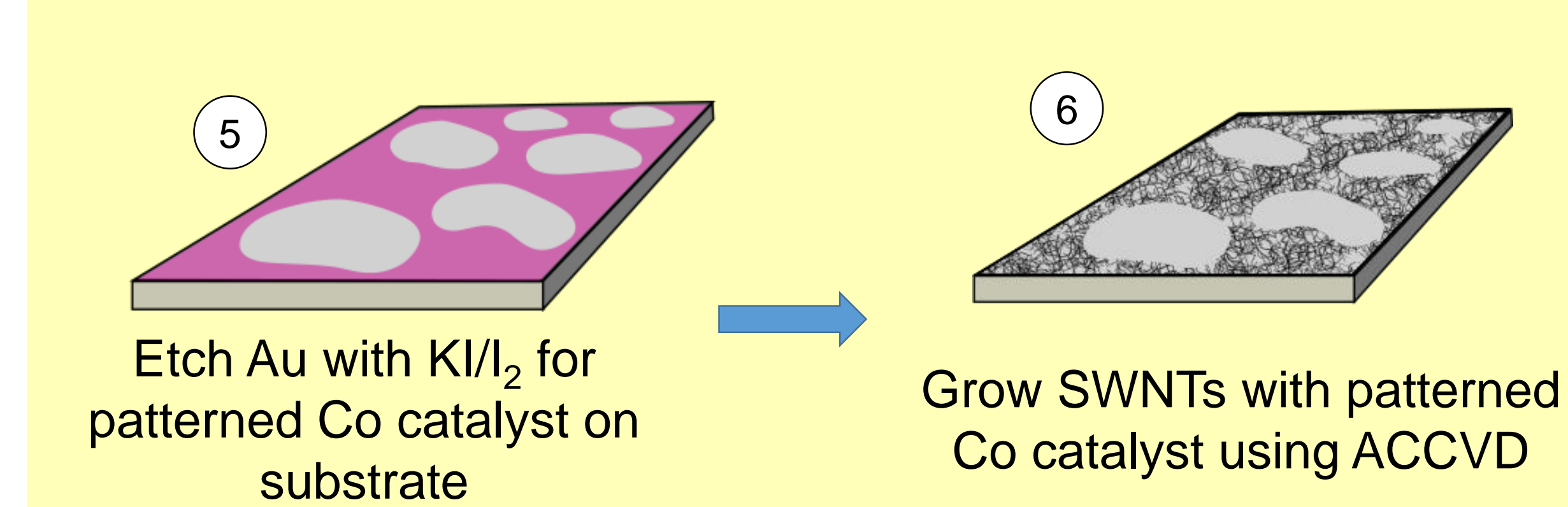
Fabrication Process



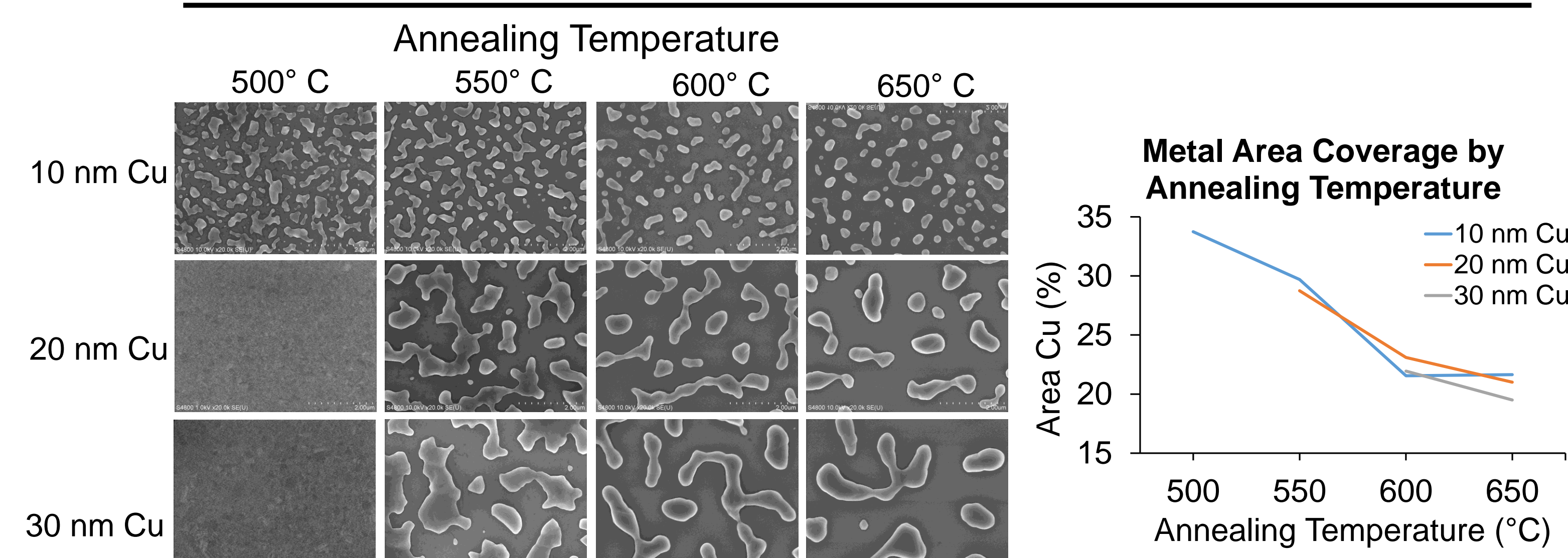
Method 1: Etch Cu After SWNT Growth



Method 2: Etch Au Before SWNT Growth

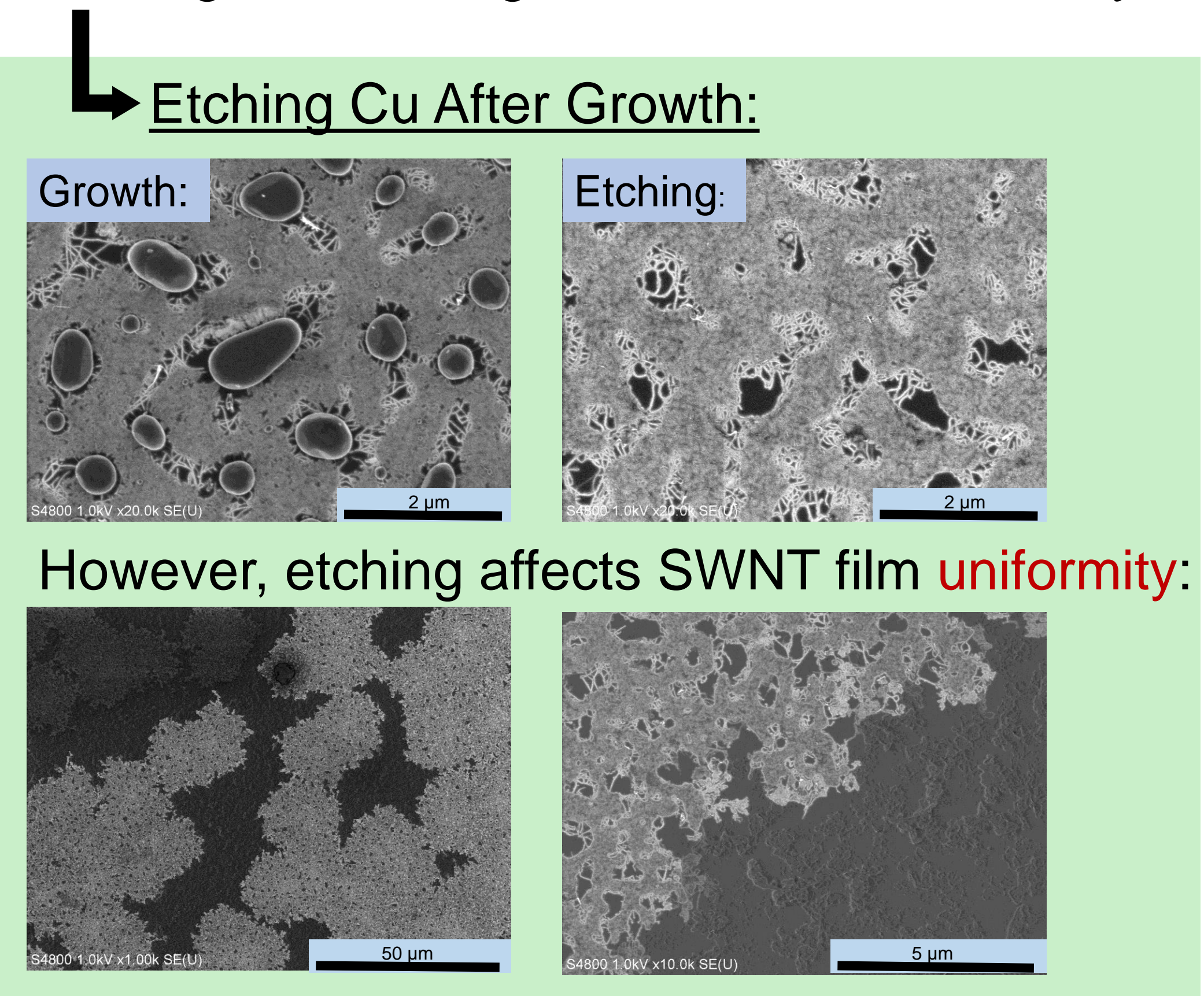


Self-Assembled Metal Masks



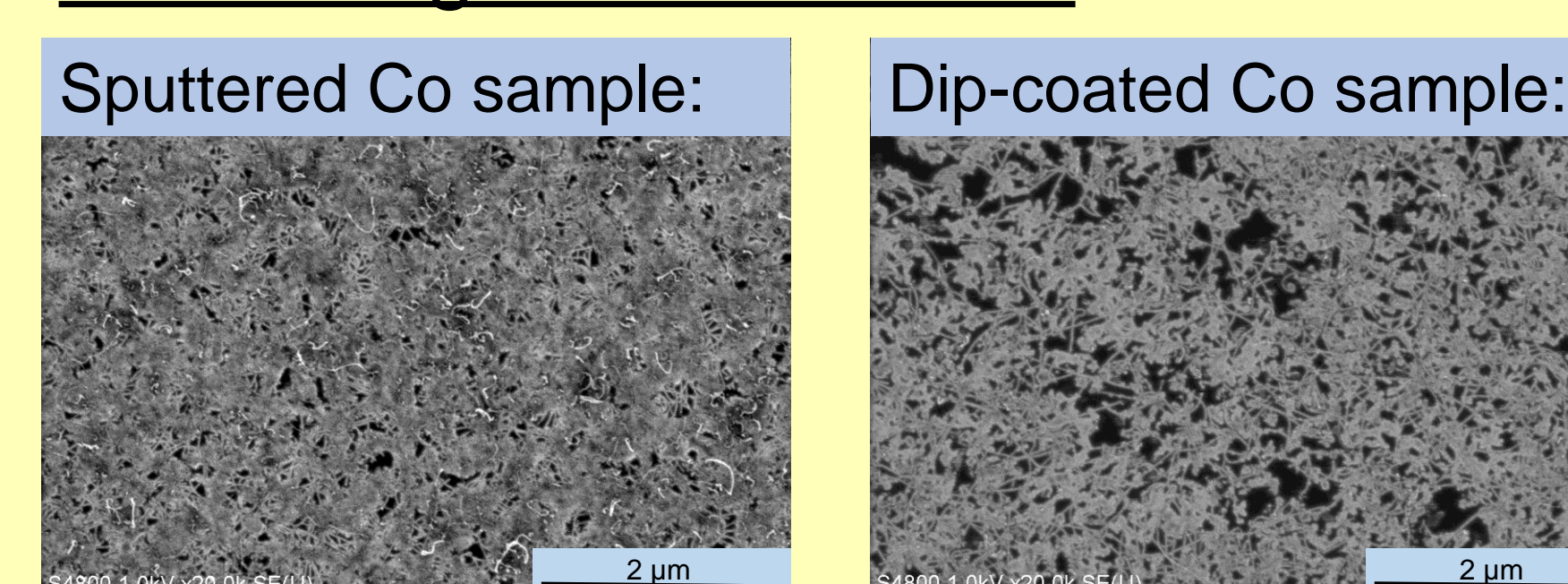
Results

Etching Cu before growth removes Co catalyst.



Au metal mask with Co oxidation allows etching before growth.

Au Etching Before Growth:



However, low SWNT yield and particulate film indicate that etching may affect Co catalyst.

Film Characterization

- Transparency
 - Transmittance: UV-vis-NIR spectroscopy
- Conductivity
 - Sheet resistance: Four-point probe method

Co Deposition	Process	T _{550 nm} (%)	R _{sh} (kΩ/□)
Sputtered	Standard	94.0	16.2
	Au Etched	97.3	713.2
Dip-coated	Standard	83.5	3.3
	Au Etched	99.0	1933.6

Conclusions

On fabrication process:

- Metal mask coverage can be controllably varied
- Use of Au instead of Cu allows for metal etching before SWNT growth
- Pre-growth etching process may affect catalyst efficiency

On film morphology:

- Transparency increased
 - Conductivity decreased
- However, compromised catalyst's low yield may be cause of low conductivity, rather than film morphology itself.

Future Work

- Determine method to further protect Co catalyst during fabrication
- Increase control over hole size through mask coverage
- Improve SWNT quality to increase conductivity
- Implement SWNT TCF in solar cell application

References

- ¹ Cui, K.; Chiba, T.; Omiya, S.; Thurakitseree, T.; Zhao, P.; Fujii, S.; Kataura, H.; Einarsson, E.; Chiashi, S.; Maruyama, S. Self-Assembled Microhoneycomb Network of Single-Walled Carbon Nanotubes for Solar Cells. *J. Phys. Chem. Lett.* **2013**, *4*, 2571–2576.
- ² Fukaya, N.; Kim, D. Y.; Kishimoto, S.; Noda, S.; Ohno, Y. One-Step Sub-10 μm Patterning of Carbon-Nanotube Thin Films for Transparent Conductor Applications. *ACS Nano*. **2014**, *8*, 3285–3293.

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