Journal of Visualized Experiments

Growth of Gold Dendritic Nanoforests on Titanium Nitride-Coated Silicon Substrates

--Manuscript Draft--

Article Type:	Methods Article - JoVE Produced Video
Manuscript Number:	JoVE59603R2
Full Title:	Growth of Gold Dendritic Nanoforests on Titanium Nitride-Coated Silicon Substrates
Keywords:	nano; gold; titanium nitride; galvanic replacement reaction; dendrite; silicon; synthesis
Corresponding Author:	Yung-Sheng Lin National United University Miaoli , Miaoli TAIWAN
Corresponding Author's Institution:	National United University
Corresponding Author E-Mail:	linys@sunrise.hk.edu.tw
Order of Authors:	Yung-Sheng Lin
	Ming-Hua Shiao
	Jian-Jia Zeng
	Hung Ji Huang
	Bo-Huei Liao
	Yu-Hsiang Tang
Additional Information:	
Question	**Response**
Please indicate whether this article will be Standard Access or Open Access.	Standard Access (US$2,400)
Please indicate the **city, state/province, and country** where this article will be **filmed**. Please do not use abbreviations.	Hsinchu, Taiwan

TITLE:

Growth of Gold Dendritic Nanoforests on Titanium Nitride-Coated Silicon Substrates

AUTHORS AND AFFILIATIONS:

Ming-Hua Shiao[1], Jian-Jia Zeng[2], Hung Ji Huang[1], Bo-Huei Liao[1], Yu-Hsiang Tang[1], Yung-Sheng Lin[2]

[1]Instrument Technology Research Center, National Applied Research Laboratories, Hsinchu, Taiwan

[2]Department of Chemical Engineering, National United University, Miaoli, Taiwan

Email addresses of the co-authors:

Ming-Hua Shiao (mhshiao@narlabs.org.tw)

Jian-Jia Zeng (l82178253@gmail.com)

Hung Ji Huang (hjhuang@narlabs.org.tw)

Bo-Huei Liao (bohuei@narlabs.org.tw)

Yu-Hsiang Tang (sky520830@narlabs.org.tw)

Corresponding author:

Yung-Sheng Lin (linys@nuu.edu.tw)

KEYWORDS:

nano, gold, titanium nitride, silicon, galvanic replacement reaction, dendrite, synthesis

SUMMARY:

This study presents a feasible procedure for synthesizing gold dendritic nanoforests on titanium nitride/silicon substrates. The thickness of gold dendritic nanoforests increases linearly within 15 min of a synthesis reaction.

ABSTRACT:

In this study, a high-power impulse magnetron sputtering system is used to coat a flat and firm titanium nitride (TiN) film on silicon (Si) wafers, and a fluoride-assisted galvanic replacement reaction (FAGRR) is employed for the rapid and easy deposition of gold dendritic nanoforests (Au DNFs) on the TiN/Si substrates. Scanning electron microscopy (SEM) images and energy-dispersive X-ray spectroscopy patterns of TiN/Si and Au DNFs/TiN/Si samples validate that the synthesis process is accurately controlled. Under the reaction conditions in this study, the thickness of the Au DNFs increases linearly to 5.10 ± 0.20 µm within 15 min of the reaction. Therefore, the employed synthesis procedure is a simple and rapid approach for preparing Au DNFs/TiN/Si composites.

INTRODUCTION:

Gold nanoparticles have characteristic optical properties and localized surface plasmon resonances (LSPRs), depending on the size and shape of the nanoparticles[1–4]. Moreover, gold nanoparticles can significantly enhance plasmonic photocatalytic reactions[5]. Dendritic nanoforests stacked using gold nanoparticles have received considerable attention because of their noteworthy specific surface areas and robust LSPR enhancement[6–13].

TiN is an extremely hard ceramic material and has remarkable thermal, chemical, and mechanical stability. TiN has distinctive optical properties and can be used for plasmonic applications with visible-to-near-infrared light[14,15]. Research has demonstrated that TiN can produce electromagnetic field enhancements, similar to Au nanostructures[16]. The deposition of copper[17] or silver[18–20] on TiN substrates for applications has been demonstrated. However, few studies have been performed on Au/TiN composite materials for applications. Shiao et al. have recently demonstrated potential applications of Au DNFs/TiN composites for photoelectrochemical cells[21] and chemical degradation[22].

Au can be synthesized on a TiN substrate by using a FAGRR[23]. The deposition condition of Au DNFs on TiN is crucial in the performance of applications. This study examines the growth of Au DNFs on a TiN-coated Si substrate.

PROTOCOL:

1) Sample preparation

1.1) TiN substrate preparation using a high-power impulse magnetron sputtering system

1.1.1) Cut a 4 inch n-type silicon wafer into 2 cm x 2 cm samples.

1.1.2) Wash the samples using acetone, isopropanol, and deionized water.

1.1.3) Dry them using an N_2 spray for 5 min.

1.1.4) Place the washed Si samples in a sample holder and place the sample holder into a high-power impulse magnetron sputtering (HIPIMS) chamber.

1.1.5) Place a titanium target with a diameter of 4 inches on a sputtering cathode.

1.1.6) Reduce the chamber pressure to less than 8 x 10^{-6} Torr by using a mechanical pump and cryopump.

1.1.7) Use HIPIMS to deposit a Ti layer on a silicon wafer and deposit a TiN layer on the Ti layer. See **Table 1** for the deposition parameters of Ti and TiN layers in HIPIMS.

1.2) Au DNF preparation on TiN/Si substrates

1.2.1) Place 24 mL of a reactant solution comprising 10 mM chloroauric acid ($HAuCl_4$) and buffered oxide etchant solution comprising 11.3% NH_4F and 2.3% HF into a Teflon container measuring 5 cm x 5 cm x 5 cm.

1.2.2) Dip the substrates into the mixture solution for 3 min.

1.2.3) Remove the sample and wash it using deionized water.

1.2.4) Dry the sample using the N_2 spray and then incubate it at 120 °C for 5 min to obtain Au DNFs/TiN/Si samples.

1.2.5) Repeat the Au DNF preparation 10x.

2) Sample examination

2.1) Scanning electron microscopy analyses

2.1.1) Cut the sample into 0.4 cm x 0.8 cm with a tungsten pen.

2.1.2) Coat a thin Au film on the sample by an ion sputter coater for 50 s and clean it using the N_2 spray.

2.1.3) Place the prepared sample into a scanning electron microscopy (SEM) instrument.

2.1.4) Obtain SEM images by the scanning electron microscope and conduct element analysis[21,22].

2.2) X-ray diffraction analyses

2.2.1) Place the sample into an X-ray diffraction (XRD) instrument.

2.2.2) Obtain XRD patterns[21,22].

REPRESENTATIVE RESULTS:

Figure 1 depicts images of the Au DNFs/TiN/Si sample preparations. The silicon wafer was silvery white (**Figure 1a**). TiN/Si was golden yellow and had a homogeneous surface (**Figure 1b**), which indicated the uniform TiN coating on the silicon wafer. Au DNFs/TiN/Si was yellowish brown and less homogeneous on the surface (**Figure 1c**) because of the random distribution of Au DNFs.

Figure 2 presents the plan and cross-sectional SEM images of Au DNFs deposited on the TiN/Si substrates. The TiN layer had a uniform surface (**Figure 2a**), and the thickness of the TiN layer was approximately 300 nm (**Figure 2b**). At 1 min, small Au nuclei were observed everywhere (**Figure 2c**), some of which developed into a large nucleus similar to a sea urchin (**Figure 2d**). A single tree-like structure was formed at 3 min (**Figure 2e,f**), and these branching were observed to overlap at 5 min (**Figure 2g,h**). At 10 min, Au DNFs formed and covered the entire TiN layer (**Figure 2i,j**). At 15 min, dense Au DNFs were formed (**Figure 2k**), and the thickness of the DNFs reached 5 μm (**Figure 2l**).

Figure 3 shows the energy-dispersive X-ray spectroscopy (EDS) analysis results of TiN/Si and Au DNFs/TiN/Si. The indicated elements agreed with the synthesis procedure. Furthermore, the evident peaks could validate that the coating of TiN and the synthesis of Au DNFs were not polluted.

Figure 4 illustrates the variation of the thickness of the Au DNFs on the TiN/Si substrate with FAGRR time. The thickness of the Au DNFs increased linearly with synthesis time. The linear

equation on the thickness and synthesis time, which ranged from 1 to 15 min, was expressed as follows: $y = 0.296t + 0.649$.

Figure 5 shows the XRD patterns of samples obtained by different deposition times. A strong (111) orientation of Au peaks was identified. The sharp cubic Au patterns, Au(111), Au(200), Au(220), and Au(311), agreed with JCPDS 04-0784. The increase in Au peaks with the deposition time corresponded to the growth of Au DNFs on the TiN/Si substrate. On the other hand, TiN peaks, namely TiN(111), TiN(200), TiN(220), and TiN(311), were evident at 1 min deposition, agreeing with JCPDS 38-1420. After 1 min, the signals of TiN gradually disappeared because the TiN/Si substrate was gradually covered by Au DNFs. These XRD results corresponded to previous reports[21,22].

FIGURE AND TABLE LEGENDS:

Table 1: Conditions for preparing Ti and TiN. HIPIMS parameters for the deposition of Ti and TiN layers on a silicon wafer.

Figure 1: Sample appearance. Preparation of a 2 cm x 2 cm sample of (**a**) a silicon wafer, (**b**) TiN/Si, and (**c**) Au DNFs/TiN/Si.

Figure 2: SEM pictures of samples. The SEM overhead and cross-section views of Au DNFs deposited on the TiN/Si substrates at (**a** and **b**) 0 min; (**c** and **d**) 1 min; (**e** and **f**) 3 min; (**g** and **h**) 5 min; (**i** and **j**) 10 min; (**k** and **l**) 15 min.

Figure 3: Elemental analysis. EDS spectrum of (**a**) TiN/Si and (**b**) Au DNFs/TiN/Si.

Figure 4: Au DNF thickness. The thickness of Au DNFs on TiN/Si substrate at various synthesis times ($n = 10$)

Figure 5: XRD patterns of samples. XRD patterns of Au DNFs on TiN/Si substrate at different synthesis times.

DISCUSSION:

In this study, Au DNFs with multiple branch sizes were decorated on the surface of TiN/Si by using FAGRR. The deposition of the Au DNFs could be directly identified by a significant change in color. The thickness of the Au DNFs on TiN/Si increased to 5.10 ± 0.20 µm within 15 min, and this increase in thickness can be expressed using the following linear equation: $y = 0.296t + 0.649$, where the time varied from 1 to 15 min.

In FAGRR, the metal deposition is affected by the composition and the pH of the solution[23]. The deposition rate increases with the density of substrate surface defects. The thickness of the TiN layer decreases as the replacement reaction time increases. It is easy to remove Au DNFs from the TiN/Si substrates if the thickness of Au DNFs is thick enough.

Galvanic displacement reaction is more favorable for a metal with a higher redox potential[23]. In this study, the proposed facile and rapid electroless deposition process provides a

feasible approach for preparing Au/TiN/Si composites which can be used as visible-light photocatalysts[21,22]. Using the same protocol, it is also possible to fabricate Au DNFs on other substrates, such as TiN/SiO_2/Si, TiN/glass, TiN/ITO, and TiN/FTO, for applications in the future.

ACKNOWLEDGMENTS:

This work was supported by the Ministry of Science and Technology, Taiwan, under contract numbers MOST 105-2221-E-492-003-MY2 and MOST 107-2622-E-239-002-CC3.

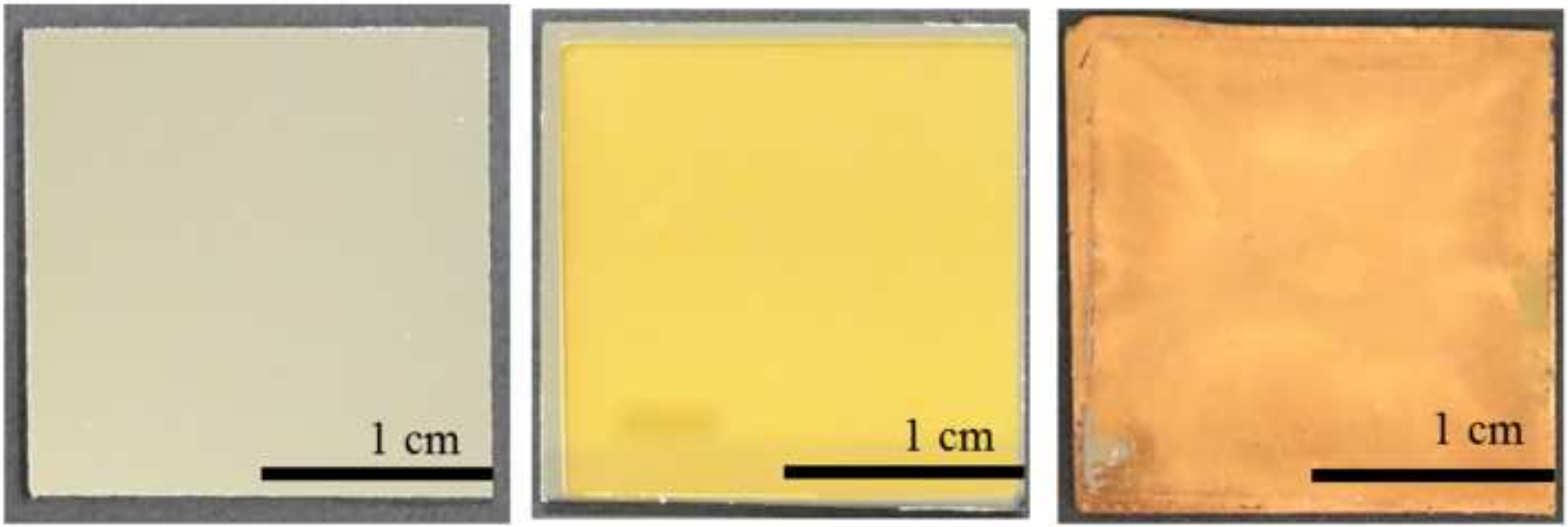
DISCLOSURES

The authors have nothing to disclose.

REFERENCES:

1. Nehl, C.L., Hafner, J.H. Shape-dependent plasmon resonances of gold nanoparticles. *Journal of Materials Chemistry*. **18**(21), 2415-2419 (2008).
2. Auguié, B., Barnes, W.L. Collective resonances in gold nanoparticle arrays. *Physical Review Letters*. **101** (14), 143902 (2008).
3. Sakai, N., Fujiwara, Y., Arai, M., Yu, K., Tatsuma, T. Electrodeposition of gold nanoparticles on ITO: Control of morphology and plasmon resonance-based absorption and scattering. *Journal of Electroanalytical Chemistry*. **628** (1-2), 7-15 (2009).
4. Shiao, M.H., Lai, C.P., Liao, B.H., Lin, Y.S. Effect of photoillumination on gold-nanoparticle-assisted chemical etching of silicon. *Journal of Nanomaterials*. **2018**, 5479605 (2018).
5. Ayati, A. et al. Photocatalytic degradation of nitrobenzene by gold nanoparticles decorated polyoxometalate immobilized TiO_2 nanotubes. *Separation and Purification Technology*. **171**, 62-68 (2016).
6. Huang, T., Meng, F., Qi, L. Controlled synthesis of dendritic gold nanostructures assisted by supramolecular complexes of surfactant with cyclodextrin. *Langmuir*. **26** (10), 7582-7589 (2009).
7. Lahiri, A., Wen, R., Kuimalee, S., Kobayashi, S.I., Park, H. One-step growth of needle and dendritic gold nanostructures on silicon for surface enhanced Raman scattering. *CrystEngComm*. **14** (4), 1241-1246 (2012).
8. Lahiri, A., Wen, R., Kobayashi, S.I., Wang, P., Fang, Y. Unique and unusual pattern demonstrating the crystal growth through bubble formation. *Crystal Growth & Design*. **12** (3), 1666-1670 (2012).
9. Lahiri, A. et al. Photo-assisted control of gold and silver nanostructures on silicon and its SERRS effect. *Journal of Physics D: Applied Physics*. **46** (27), 275303 (2013).
10. Lv, Z.Y. et al. Facile and controlled electrochemical route to three-dimensional hierarchical dendritic gold nanostructures. *Electrochimica Acta*. **109**, 136-144 (2013).
11. Dutta, S. et al. Mesoporous gold and palladium nanoleaves from liquid–liquid interface: enhanced catalytic activity of the palladium analogue toward hydrazine-assisted room-temperature 4-nitrophenol reduction. *ACS Applied Materials & Interfaces*. **6** (12), 9134-9143 (2014).
12. Lin, C.T. et al. Rapid fabrication of three-dimensional gold dendritic nanoforests for visible light-enhanced methanol oxidation. *Electrochimica Acta*. **192**, 15-21 (2016).
13. Lahiri, A., Kobayashi, S.I. Electroless deposition of gold on silicon and its potential applications. *Surface Engineering*. **32** (5), 321-337 (2016).
14. White, N. et al. Surface/interface analysis and optical properties of RF sputter-deposited nanocrystalline titanium nitride thin films. *Applied Surface Science*. **292**, 74-85 (2014).

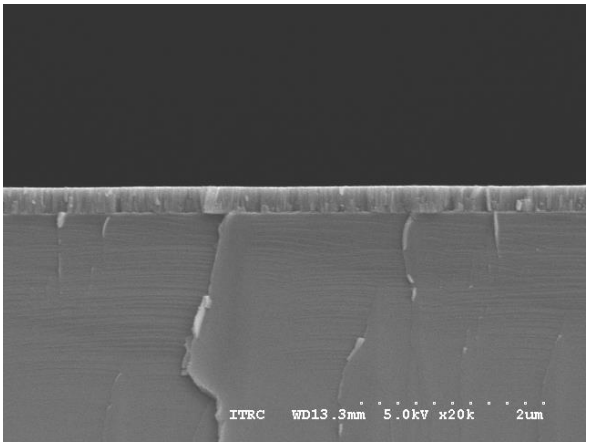
15. Zhao, J. et al. Surface enhanced Raman scattering substrates based on titanium nitride nanorods. *Optical Materials*. **47**, 219-224 (2015).
16. Lorite, I., Serrano, A., Schwartzberg, A., Bueno, J., Costa-Krämer, J.L. Surface enhanced Raman spectroscopy by titanium nitride non-continuous thin films. *Thin Solid Films*. **531**, 144-146 (2013).
17. O'Kelly, J.P. et al. Room temperature electroless plating copper seed layer process for damascene interlevel metal structures. *Microelectronic Engineering*. **50** (1), 473-479 (2000).
18. Cesiulis, H., Ziomek-Moroz, M. Electrocrystallization and electrodeposition of silver on titanium nitride. *Journal of Applied Electrochemistry*. **30** (11), 1261-1268 (2000).
19. Wu, Y., Chen, W.C., Fong, H.P., Wan, C.C., Wang, Y.Y. Displacement reactions between metal ions and nitride barrier layer/silicon substrate. *Journal of the Electrochemical Society*. **149** (5), G309-G317 (2002).
20. Koo, H.C., Ahn, E.J., Kim, J.J. Direct-electroplating of Ag on pretreated TiN surfaces. *Journal of the Electrochemical Society*. **155** (1), D10-D13 (2008).
21. Shiao, M.H. et al. Novel gold dendritic nanoflowers deposited on titanium nitride for photoelectrochemical cells. *Journal of Solid State Electrochemistry*. **22** (10), 3077-3084 (2018).
22. Shiao, M.H., Lin, C.T., Zeng, J.J., Lin, Y.S. Novel gold dendritic nanoforests combined with titanium nitride for visible-light-enhanced chemical degradation. *Nanomaterials.* **8** (5), 282 (2018).
23. Carraro, C., Maboudian, R., Magagnin, L. Metallization and nanostructuring of semiconductor surfaces by galvanic displacement processes. *Surface Science Reports*. **62** (12), 499-525 (2007).



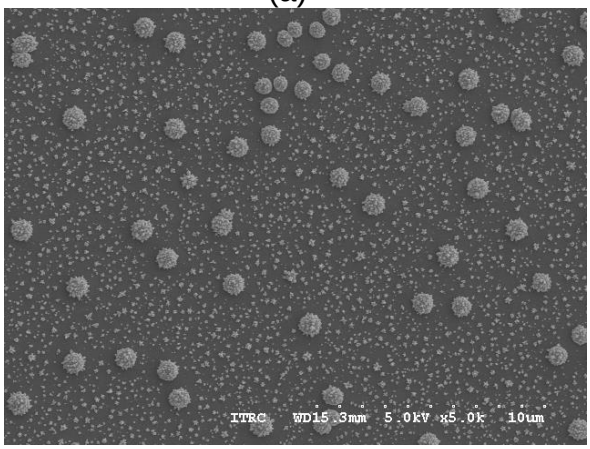
1(a) 1(b) 1(c)

Figure 2

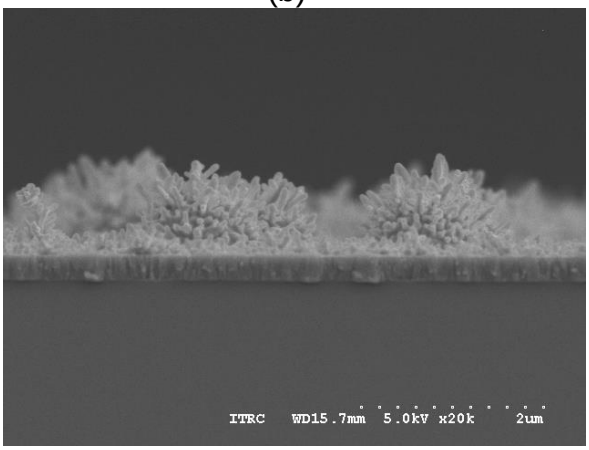
(a)



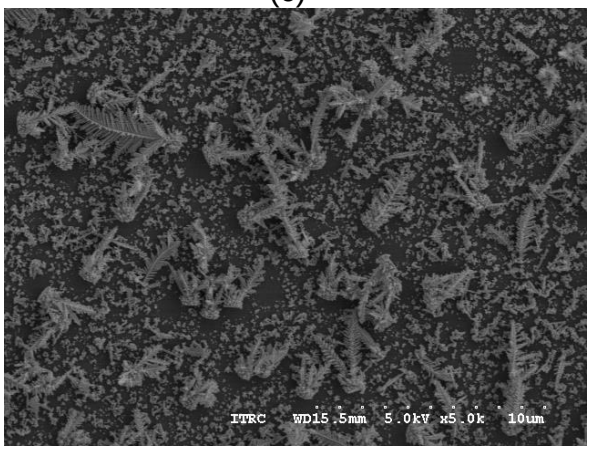
(b)



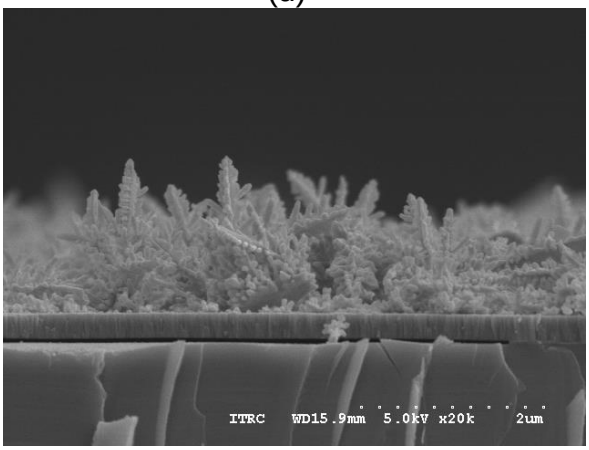
(c)



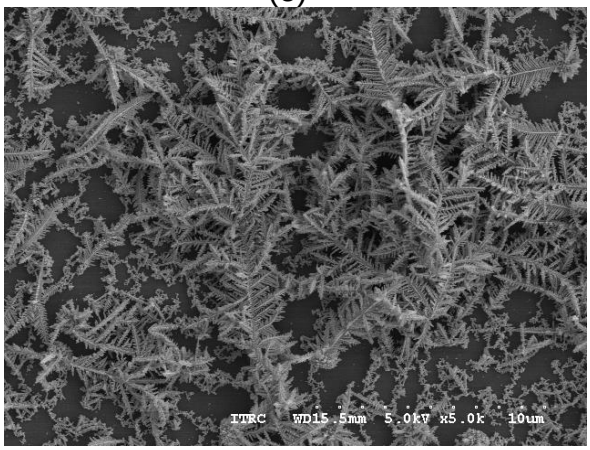
(d)



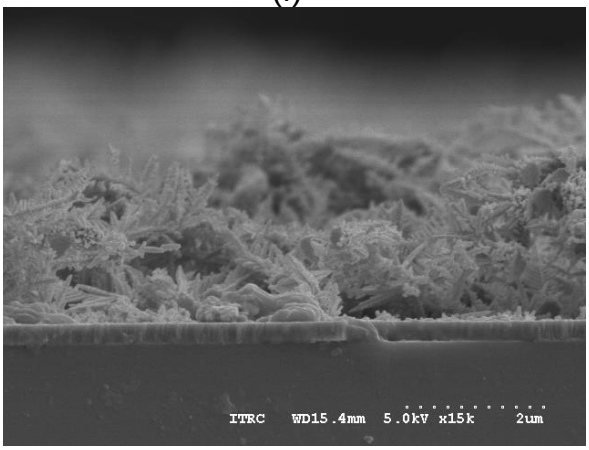
(e)



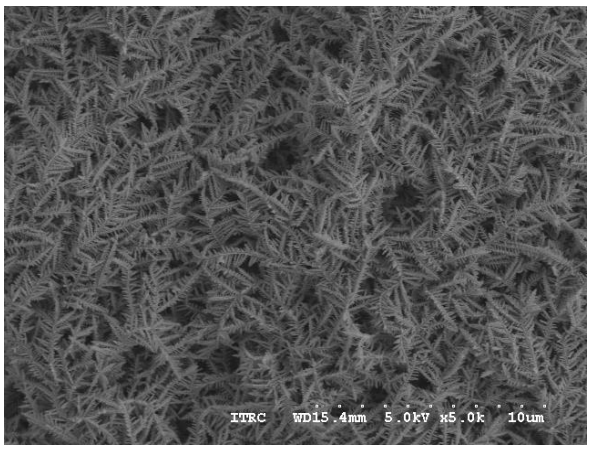
(f)



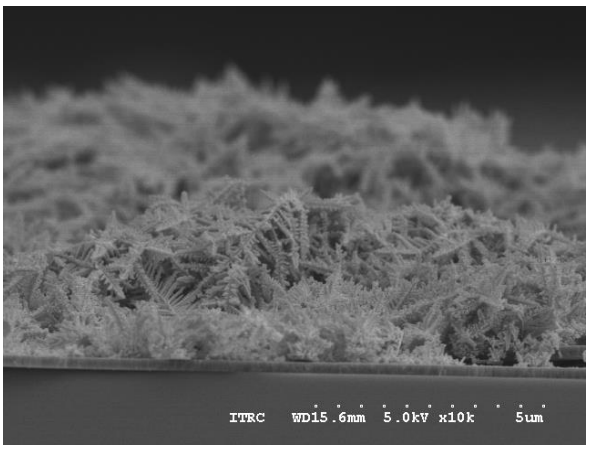
(g)



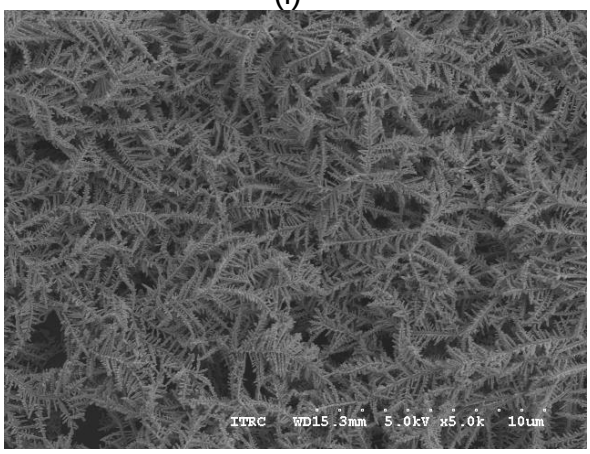
(h)


ITRC WD15.4mm 5.0kV x5.0k 10um

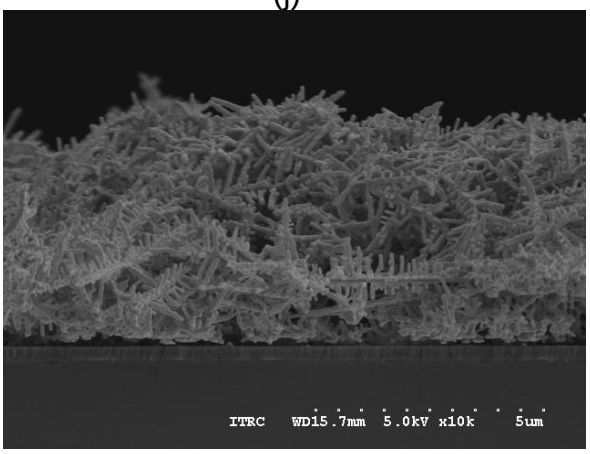
(i)


ITRC WD15.6mm 5.0kV x10k 5um

(j)


ITRC WD15.3mm 5.0kV x5.0k 10um

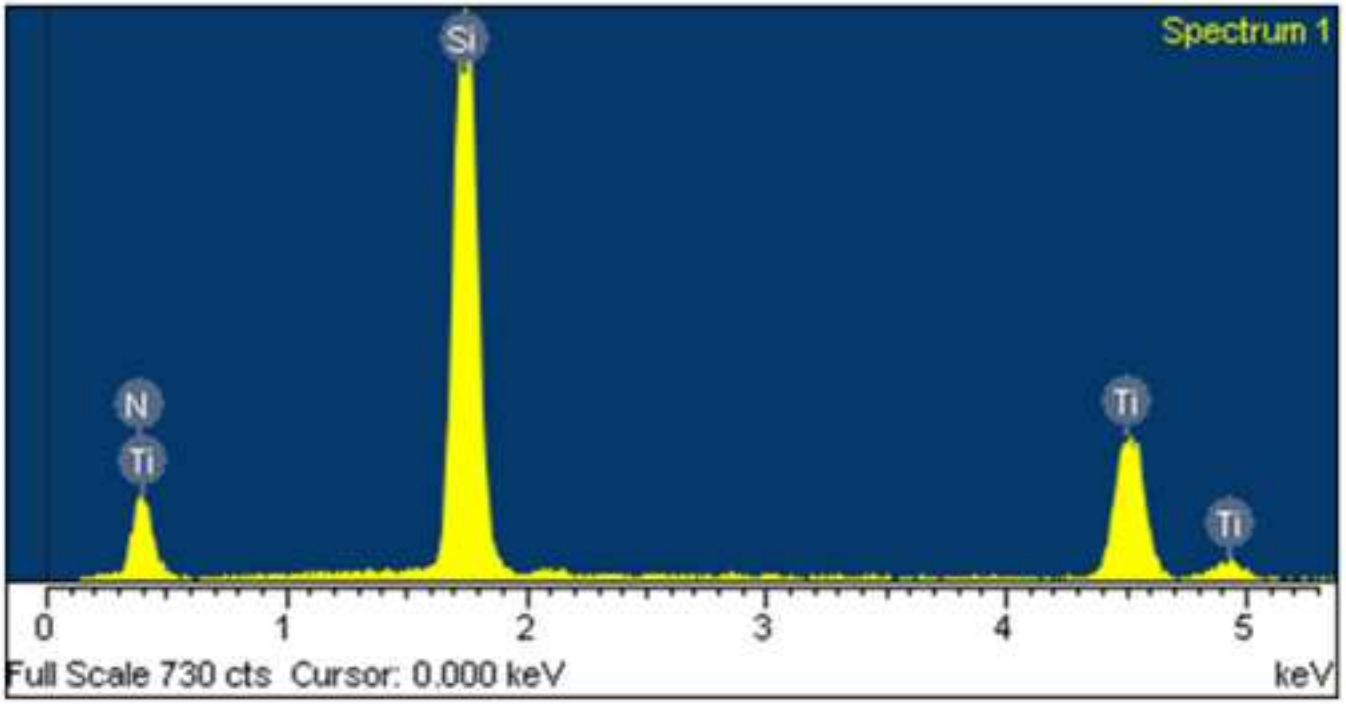
(k)


ITRC WD15.7mm 5.0kV x10k 5um

(l)

Figure 3

3(a)



3(b)

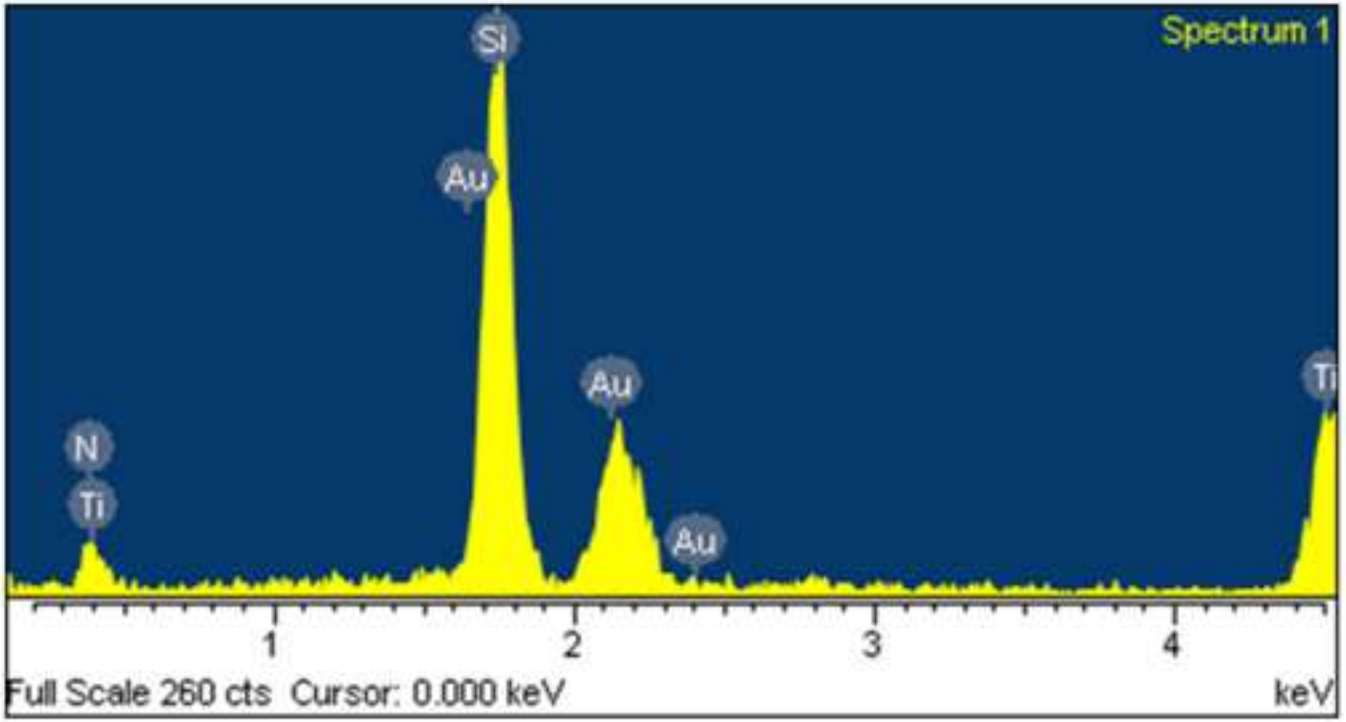


Figure 4

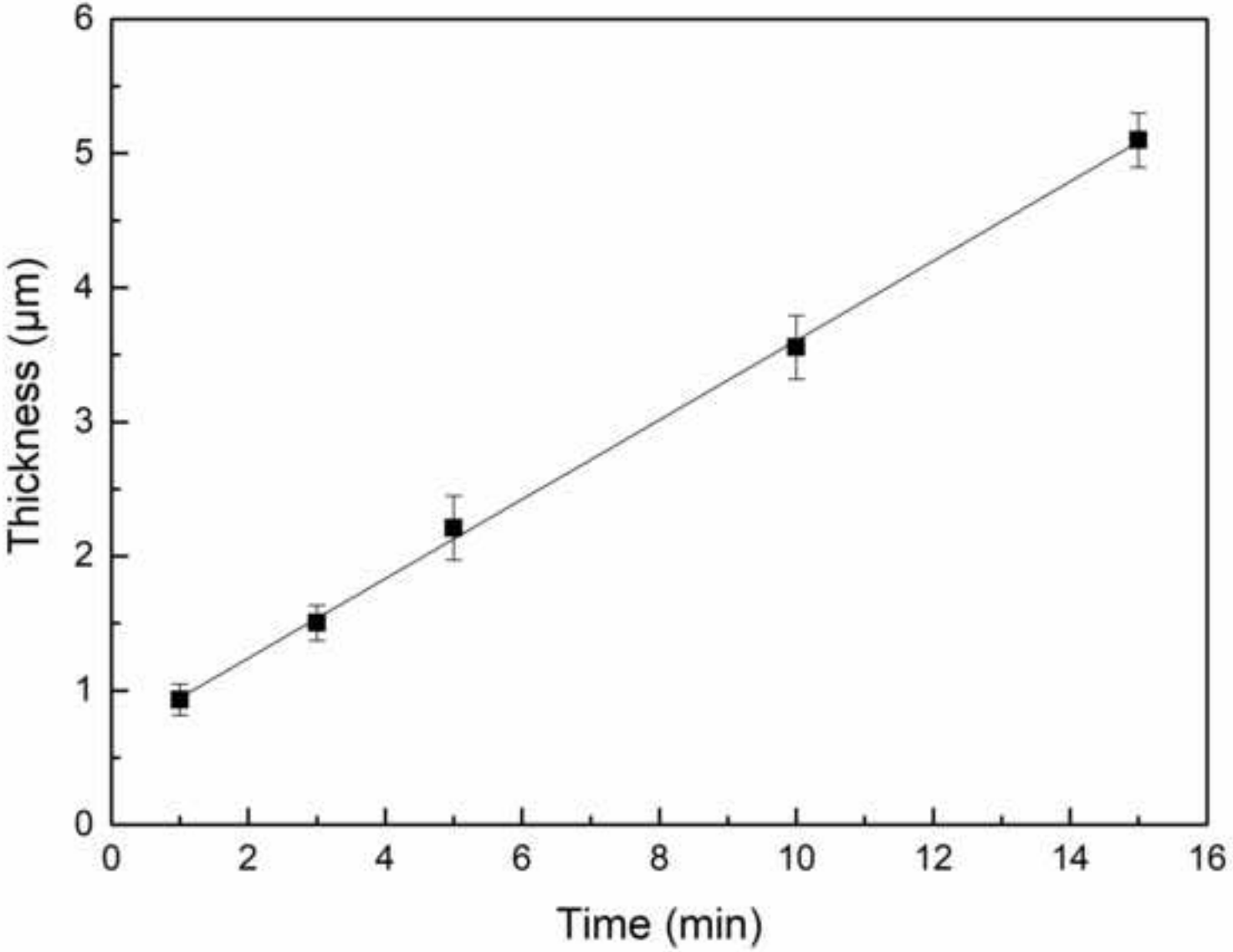


Figure 5

Click here to access/download;Figure;5.tif

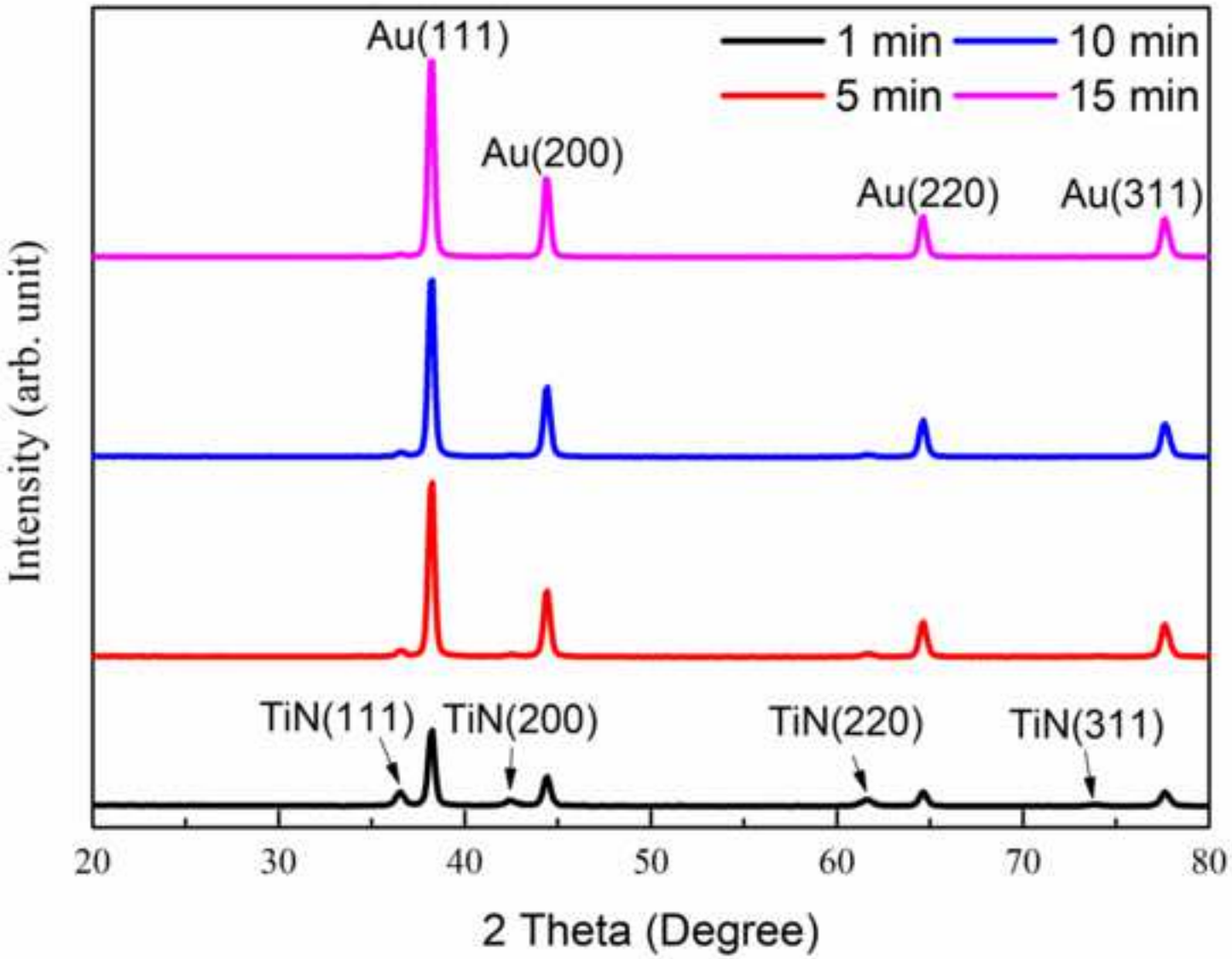


Table 1

Substrate	DC power (W)	Impulse duration (μs)	Flow rate of Ar (sccm)	Flow rate of N_2 (sccm)
Ti layer	250	90	20	-
TiN layer	300	1000	30	1.5

Name of Material/Equipment	Company	Catalog Number
Acetone	Dinhaw Enterprise Co. Ltd.,Taipei, Taiwan	
Isopropanol	Echo Chemical Co. Ltd., Miaoli, Taiwan	TG-078-000000-75NL
Buffered Oxide Etch	Uni-onward Corp., Hsinchu, Taiwan	UR-BOE-1EA
Chloroauric Acid	Alfa Aesar., Heysham, United Kingdom	36400.03
N-Type Silicon Wafer	Summit-Tech Company, Hsinchu, Taiwan	
High-Power Impulse Magnetron Sputtering System (HiPIMS)	Melec GmbH, Germany	
Scanning Electron Microscope (SEM)	JEOL, Japan	
Ion Sputter Coater	Hitachi, Japan	
X-Ray Diffractometer (XRD)	PANalytical, The Netherlands	

Comments/Description
SPIK2000A
JSM-7800F
E101
X'Pert PRO MRD

jove JOURNAL OF VISUALIZED EXPERIMENTS
1 Alewife Center #200
Cambridge, MA 02140
tel. 617.945.9051
www.jove.com

ARTICLE AND VIDEO LICENSE AGREEMENT

Title of Article: Growth of Gold Dendritic Nanoforests on Titanium Nitride-Coated Silicon Substrates

Author(s): Ming-Hua Shiao, Jian-Jia Zeng, Hung Ji Huang, Bo-Huei Liao, Yu-Hsiang Tang, Yung-Sheng Lin

Item 1: The Author elects to have the Materials be made available (as described at http://www.jove.com/publish) via:

☑ Standard Access ☐ Open Access

Item 2: Please select one of the following items:

☑ The Author is **NOT** a United States government employee.

☐ The Author is a United States government employee and the Materials were prepared in the course of his or her duties as a United States government employee.

☐ The Author is a United States government employee but the Materials were NOT prepared in the course of his or her duties as a United States government employee.

ARTICLE AND VIDEO LICENSE AGREEMENT

1. **Defined Terms.** As used in this Article and Video License Agreement, the following terms shall have the following meanings: "**Agreement**" means this Article and Video License Agreement; "**Article**" means the article specified on the last page of this Agreement, including any associated materials such as texts, figures, tables, artwork, abstracts, or summaries contained therein; "**Author**" means the author who is a signatory to this Agreement; "**Collective Work**" means a work, such as a periodical issue, anthology or encyclopedia, in which the Materials in their entirety in unmodified form, along with a number of other contributions, constituting separate and independent works in themselves, are assembled into a collective whole; "**CRC License**" means the Creative Commons Attribution-Non Commercial-No Derivs 3.0 Unported Agreement, the terms and conditions of which can be found at: http://creativecommons.org/licenses/by-nc-nd/3.0/legalcode; "**Derivative Work**" means a work based upon the Materials or upon the Materials and other pre-existing works, such as a translation, musical arrangement, dramatization, fictionalization, motion picture version, sound recording, art reproduction, abridgment, condensation, or any other form in which the Materials may be recast, transformed, or adapted; "**Institution**" means the institution, listed on the last page of this Agreement, by which the Author was employed at the time of the creation of the Materials; "**JoVE**" means MyJove Corporation, a Massachusetts corporation and the publisher of The Journal of Visualized Experiments; "**Materials**" means the Article and / or the Video; "**Parties**" means the Author and JoVE; "**Video**" means any video(s) made by the Author, alone or in conjunction with any other parties, or by JoVE or its affiliates or agents, individually or in collaboration with the Author or any other parties, incorporating all or any portion of the Article, and in which the Author may or may not appear.

2. **Background.** The Author, who is the author of the Article, in order to ensure the dissemination and protection of the Article, desires to have the JoVE publish the Article and create and transmit videos based on the Article. In furtherance of such goals, the Parties desire to memorialize in this Agreement the respective rights of each Party in and to the Article and the Video.

3. **Grant of Rights in Article.** In consideration of JoVE agreeing to publish the Article, the Author hereby grants to JoVE, subject to **Sections 4** and **7** below, the exclusive, royalty-free, perpetual (for the full term of copyright in the Article, including any extensions thereto) license (a) to publish, reproduce, distribute, display and store the Article in all forms, formats and media whether now known or hereafter developed (including without limitation in print, digital and electronic form) throughout the world, (b) to translate the Article into other languages, create adaptations, summaries or extracts of the Article or other Derivative Works (including, without limitation, the Video) or Collective Works based on all or any portion of the Article and exercise all of the rights set forth in (a) above in such translations, adaptations, summaries, extracts, Derivative Works or Collective Works and(c) to license others to do any or all of the above. The foregoing rights may be exercised in all media and formats, whether now known or hereafter devised, and include the right to make such modifications as are technically necessary to exercise the rights in other media and formats. If the "Open Access" box has been checked in **Item 1** above, JoVE and the Author hereby grant to the public all such rights in the Article as provided in, but subject to all limitations and requirements set forth in, the CRC License.

jove JOURNAL OF VISUALIZED EXPERIMENTS
1 Alewife Center #200
Cambridge, MA 02140
tel. 617.945.9051
www.jove.com

ARTICLE AND VIDEO LICENSE AGREEMENT

4. **Retention of Rights in Article.** Notwithstanding the exclusive license granted to JoVE in **Section 3** above, the Author shall, with respect to the Article, retain the non-exclusive right to use all or part of the Article for the non-commercial purpose of giving lectures, presentations or teaching classes, and to post a copy of the Article on the Institution's website or the Author's personal website, in each case provided that a link to the Article on the JoVE website is provided and notice of JoVE's copyright in the Article is included. All non-copyright intellectual property rights in and to the Article, such as patent rights, shall remain with the Author.

5. **Grant of Rights in Video – Standard Access.** This **Section 5** applies if the "Standard Access" box has been checked in **Item 1** above or if no box has been checked in **Item 1** above. In consideration of JoVE agreeing to produce, display or otherwise assist with the Video, the Author hereby acknowledges and agrees that, Subject to **Section 7** below, JoVE is and shall be the sole and exclusive owner of all rights of any nature, including, without limitation, all copyrights, in and to the Video. To the extent that, by law, the Author is deemed, now or at any time in the future, to have any rights of any nature in or to the Video, the Author hereby disclaims all such rights and transfers all such rights to JoVE.

6. **Grant of Rights in Video – Open Access.** This **Section 6** applies only if the "Open Access" box has been checked in **Item 1** above. In consideration of JoVE agreeing to produce, display or otherwise assist with the Video, the Author hereby grants to JoVE, subject to **Section 7** below, the exclusive, royalty-free, perpetual (for the full term of copyright in the Article, including any extensions thereto) license (a) to publish, reproduce, distribute, display and store the Video in all forms, formats and media whether now known or hereafter developed (including without limitation in print, digital and electronic form) throughout the world, (b) to translate the Video into other languages, create adaptations, summaries or extracts of the Video or other Derivative Works or Collective Works based on all or any portion of the Video and exercise all of the rights set forth in (a) above in such translations, adaptations, summaries, extracts, Derivative Works or Collective Works and (c) to license others to do any or all of the above. The foregoing rights may be exercised in all media and formats, whether now known or hereafter devised, and include the right to make such modifications as are technically necessary to exercise the rights in other media and formats. For any Video to which this **Section 6** is applicable, JoVE and the Author hereby grant to the public all such rights in the Video as provided in, but subject to all limitations and requirements set forth in, the CRC License.

7. **Government Employees.** If the Author is a United States government employee and the Article was prepared in the course of his or her duties as a United States government employee, as indicated in **Item 2** above, and any of the licenses or grants granted by the Author hereunder exceed the scope of the 17 U.S.C. 403, then the rights granted hereunder shall be limited to the maximum rights permitted under such statute. In such case, all provisions contained herein that are not in conflict with such statute shall remain in full force and effect, and all provisions contained herein that do so conflict shall be deemed to be amended so as to provide to JoVE the maximum rights permissible within such statute.

8. **Protection of the Work.** The Author(s) authorize JoVE to take steps in the Author(s) name and on their behalf if JoVE believes some third party could be infringing or might infringe the copyright of either the Author's Article and/or Video.

9. **Likeness, Privacy, Personality.** The Author hereby grants JoVE the right to use the Author's name, voice, likeness, picture, photograph, image, biography and performance in any way, commercial or otherwise, in connection with the Materials and the sale, promotion and distribution thereof. The Author hereby waives any and all rights he or she may have, relating to his or her appearance in the Video or otherwise relating to the Materials, under all applicable privacy, likeness, personality or similar laws.

10. **Author Warranties.** The Author represents and warrants that the Article is original, that it has not been published, that the copyright interest is owned by the Author (or, if more than one author is listed at the beginning of this Agreement, by such authors collectively) and has not been assigned, licensed, or otherwise transferred to any other party. The Author represents and warrants that the author(s) listed at the top of this Agreement are the only authors of the Materials. If more than one author is listed at the top of this Agreement and if any such author has not entered into a separate Article and Video License Agreement with JoVE relating to the Materials, the Author represents and warrants that the Author has been authorized by each of the other such authors to execute this Agreement on his or her behalf and to bind him or her with respect to the terms of this Agreement as if each of them had been a party hereto as an Author. The Author warrants that the use, reproduction, distribution, public or private performance or display, and/or modification of all or any portion of the Materials does not and will not violate, infringe and/or misappropriate the patent, trademark, intellectual property or other rights of any third party. The Author represents and warrants that it has and will continue to comply with all government, institutional and other regulations, including, without limitation all institutional, laboratory, hospital, ethical, human and animal treatment, privacy, and all other rules, regulations, laws, procedures or guidelines, applicable to the Materials, and that all research involving human and animal subjects has been approved by the Author's relevant institutional review board.

11. **JoVE Discretion.** If the Author requests the assistance of JoVE in producing the Video in the Author's facility, the Author shall ensure that the presence of JoVE employees, agents or independent contractors is in accordance with the relevant regulations of the Author's institution. If more than one author is listed at the beginning of this Agreement, JoVE may, in its sole

jove JOURNAL OF VISUALIZED EXPERIMENTS
1 Alewife Center #200
Cambridge, MA 02140
tel. 617.945.9051
www.jove.com

ARTICLE AND VIDEO LICENSE AGREEMENT

discretion, elect not take any action with respect to the Article until such time as it has received complete, executed Article and Video License Agreements from each such author. JoVE reserves the right, in its absolute and sole discretion and without giving any reason therefore, to accept or decline any work submitted to JoVE. JoVE and its employees, agents and independent contractors shall have full, unfettered access to the facilities of the Author or of the Author's institution as necessary to make the Video, whether actually published or not. JoVE has sole discretion as to the method of making and publishing the Materials, including, without limitation, to all decisions regarding editing, lighting, filming, timing of publication, if any, length, quality, content and the like.

12. **Indemnification.** The Author agrees to indemnify JoVE and/or its successors and assigns from and against any and all claims, costs, and expenses, including attorney's fees, arising out of any breach of any warranty or other representations contained herein. The Author further agrees to indemnify and hold harmless JoVE from and against any and all claims, costs, and expenses, including attorney's fees, resulting from the breach by the Author of any representation or warranty contained herein or from allegations or instances of violation of intellectual property rights, damage to the Author's or the Author's institution's facilities, fraud, libel, defamation, research, equipment, experiments, property damage, personal injury, violations of institutional, laboratory, hospital, ethical, human and animal treatment, privacy or other rules, regulations, laws, procedures or guidelines, liabilities and other losses or damages related in any way to the submission of work to JoVE, making of videos by JoVE, or publication in JoVE or elsewhere by JoVE. The Author shall be responsible for, and shall hold JoVE harmless from, damages caused by lack of sterilization, lack of cleanliness or by contamination due to the making of a video by JoVE its employees, agents or independent contractors. All sterilization, cleanliness or decontamination procedures shall be solely the responsibility of the Author and shall be undertaken at the Author's expense. All indemnifications provided herein shall include JoVE's attorney's fees and costs related to said losses or damages. Such indemnification and holding harmless shall include such losses or damages incurred by, or in connection with, acts or omissions of JoVE, its employees, agents or independent contractors.

13. **Fees.** To cover the cost incurred for publication, JoVE must receive payment before production and publication of the Materials. Payment is due in 21 days of invoice. Should the Materials not be published due to an editorial or production decision, these funds will be returned to the Author. Withdrawal by the Author of any submitted Materials after final peer review approval will result in a US$1,200 fee to cover pre-production expenses incurred by JoVE. If payment is not received by the completion of filming, production and publication of the Materials will be suspended until payment is received.

14. **Transfer, Governing Law.** This Agreement may be assigned by JoVE and shall inure to the benefits of any of JoVE's successors and assignees. This Agreement shall be governed and construed by the internal laws of the Commonwealth of Massachusetts without giving effect to any conflict of law provision thereunder. This Agreement may be executed in counterparts, each of which shall be deemed an original, but all of which together shall be deemed to me one and the same agreement. A signed copy of this Agreement delivered by facsimile, e-mail or other means of electronic transmission shall be deemed to have the same legal effect as delivery of an original signed copy of this Agreement.

A signed copy of this document must be sent with all new submissions. Only one Agreement is required per submission.

CORRESPONDING AUTHOR

Name:	Yung-Sheng Lin
Department:	Chemical Engineering
Institution:	National United University
Title:	Professor
Signature:	Yung-Sheng Lin
Date:	2018.12.24

Please submit a **signed** and **dated** copy of this license by one of the following three methods:

1. Upload an electronic version on the JoVE submission site
2. Fax the document to +1.866.381.2236
3. Mail the document to JoVE / Attn: JoVE Editorial / 1 Alewife Center #200 / Cambridge, MA 02140

Editorial comments:

The manuscript has been modified and the updated manuscript, **59603_R1.docx**, is attached and located in your Editorial Manager account. **Please use the updated version to make your revisions.**

1. Please take this opportunity to thoroughly proofread the manuscript to ensure that there are no spelling or grammar issues.

Response:

Thank you very much for the comment. We have thoroughly proofread the manuscript to avoid errors.

2. Please revise the Discussion to explicitly cover the following in detail in 3-6 paragraphs with citations:

a) Critical steps within the protocol

b) Any modifications and troubleshooting of the technique

c) Any limitations of the technique

d) The significance with respect to existing methods

e) Any future applications of the technique

Response:

Thank you very much for the comment. We have revised the Discussion in detail in 3 paragraphs with citations.

3. Please ensure that the references appear as the following:

Lastname, F.I., LastName, F.I., LastName, F.I. Article Title. *Source*. **Volume** (Issue), FirstPage – LastPage, (YEAR).

Please bold the volume number.

Response:

Thank you very much for the comment. We have revised the references to meet the standard format.

4. Please combine all panels of one figure into a single image file.

Response:

Thank you very much for the comment. We have combined all panels of one figure into a single image file.

5. Please provide at least 6 keywords or phrases. Only 5 are included in the manuscript.

Response:

Thank you very much for the comment. The keywords have been provided.

6. Step 1.1.5: Diameter of 4? Should there be a unit?

Response:

Thank you very much for the comment. We have added the unit in the manuscript.

7. 2.1.2: How to coat a Au film? Please add more details.

Response:

Thank you very much for the comment. We have added more details in the manuscript.

8. 2.1.4: Add references to published material specifying how to perform the protocol action.

Response:

Thank you very much for the comment. We have added references in the manuscript.

9. 2.2.2: Add references to published material specifying how to perform the protocol action.

Response:

Thank you very much for the comment. We have added references in the manuscript.