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Title: Fabrication and Optimization of Type II Silicon Clathrate Films

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Author Questionnaire

1. We have marked your project as author-provided footage, meaning you film the video yourself and provide JoVE with the footage to edit. JoVE will not send the videographer. Please confirm that this is correct.

√ Correct

2. Interview statements: Which interview statement filming option is the most appropriate for your group? **Please select one**.

☒ Interviewees self-record interview statements. JoVE can provide support for this option.

3. Proposed interview filming date: Please indicate the proposed date that your group will **self-film** interviews: **MM/DD/YYYY**

When you are ready to submit your video files, please contact our Content Manager, Utkarsh Khare.

Current Protocol Length

Number of Steps: 16
Number of Shots: 24

Introduction

INTRODUCTION:

1.1. **Malad-Chadi Ettobi:** We present a protocol for synthesizing type II silicon clathrate films that involves two thermal annealing steps and does not require a glove box. This approach is straightforward and cost-effective.
1.1.1. INTERVIEW: Named talent says the statement above in an interview-style shot, looking slightly off-camera. *Suggested B roll: 2.7*

What are the current experimental challenges?

1.2. **Thomas Fix:** Currently, a few laboratories produce silicon clathrate films. Our goal is to share this simple two-furnace fabrication method with the scientific community, emphasizing adherence to all specified experimental safety measures.
1.2.1. INTERVIEW: Named talent says the statement above in an interview-style shot, looking slightly off-camera.

CONCLUSION:

What significant findings have you established in your field?

1.3. **Malad-Chadi Ettobi:** We successfully fabricated type II SiCL films and improved their properties through two post-synthesis treatments: thermal pressing and reactive ion etching process.
1.3.1. INTERVIEW: Named talent says the statement above in an interview-style shot, looking slightly off-camera. *Suggested B-roll: 3.2*

What research gap are you addressing with your protocol?

1.4. **Malad-Chadi Ettobi:** We employed multiple characterization techniques, including XRD, photoluminescence, and Raman spectroscopy, to confirm the successful formation of the clathrate semiconducting phase.
1.4.1. INTERVIEW: Named talent says the statement above in an interview-style shot, looking slightly off-camera. *Suggested B-roll: Figure 3*

How will your findings advance research in your field?

1.5. **Malad-Chadi Ettobi:** We believe that this work is a stepping stone for further applications of silicon clathrates into semiconductor technology.
    1.5.1. INTERVIEW: Named talent says the statement above in an interview-style shot, looking slightly off-camera.

Protocol

2. Preparation and Synthesis of SiCL

Demonstrator: Stéphane Roques

2.1. Begin by immersing the silicon substrate in a 10 percent hydrofluoric acid solution for exactly 2 minutes to remove the native silicon dioxide present on the substrate surface **[1-TXT].**

2.1.1. LAB MEDIA: Scene 5 (Experiment).MOV: 01:38 – 01:46, 03:44 – 03:54 **TXT: Use 48 % HF acid for preparing the working solution**

2.2. After exposure to hydrofluoric acid, rinse the silicon substrate thoroughly with deionized water to remove any residual acid **[1].** Using a nitrogen gun, blow-dry the substrate to eliminate remaining water droplets and prevent surface residue **[2].**

2.2.1. LAB MEDIA: Scene 5 (Experiment).MOV: 03:56 – 04:04

2.2.2. LAB MEDIA: Scene 5 (Experiment).MOV: 05:07-05:17

2.3. Using a cutter, carefully cut a piece of metallic sodium to obtain a small rectangular slice weighing approximately 0.22 grams **[1].**

2.3.1. LAB MEDIA: Scene 4 (Experiment).MOV**:** 01:00-01:10

2.4. Immediately place the sodium slice in an airtight glass container filled with anhydrous cyclohexane. Ensure that the sodium is fully immersed in the cyclohexane to prevent oxidation **[1].**

2.4.1. LAB MEDIA: Scene 4 (Experiment).MOV: 01:13-01:22.

2.5. Now, place the previously prepared sodium slice into a cleaned Inconel alloy boat **[1].** Then, position the silicon wafer directly above the sodium slice with its polished surface facing downward toward the boat **[2].**

2.5.1. LAB MEDIA: Scene 8 (Experiment).MOV: 00:57-01:01. 01:12-01:17

2.5.2. LAB MEDIA: Scene 8 (Experiment).MOV: 01:33-01:43

2.6. Carefully insert the prepared assembly into the center of a sealed stainless-steel tube and an O-ring seal, situated inside a programmable horizontal tube furnace **[1].**

2.6.1. LAB MEDIA: Scene 8 (Experiment).MOV: 01:51-02:03

2.7. Insert a high-purity tantalum wire with a diameter of 0.5 millimeters, a length of 3.4 centimeters, and 99.95 percent purity into the tube to capture trace oxygen **[1].** Seal both ends of the stainless-steel tube using fittings that allow circulation of only argon **[2].**

2.7.1. LAB MEDIA: Scene 8(Experiment).MOV: 00:30-00:48

2.7.2. LAB MEDIA: Scene 8(Experiment).MOV: 02:57-03:01, 03:20-03:30

2.8. Purge the sealed tube with argon at a constant pressure of 1.6 bar for 15 minutes to establish an inert atmosphere throughout the reaction **[1].**

2.8.1. LAB MEDIA: Scene 9 (Experiment).MOV

2.9. Then, raise the temperature of the furnace at a ramp rate of 5 degrees Celsius per minute until it reaches 600 degrees Celsius and maintain it for 19 hours **[1-TXT].**

2.9.1. LAB MEDIA: Scene 13 (Experiment).MOV: 00:00-00:16 **TXT: Allow the system to cool for 7 h**

2.10. When the furnace and tube have cooled back to room temperature, flush the system with a continuous flow of argon **[1].** Transfer the obtained samples as quickly as possible into a quartz tube and connect the tube to a dynamic vacuum furnace **[2].**

2.10.1. LAB MEDIA: Scene 9 (Experiment).MOV**:** 00:00 – 00:09

2.10.2. LAB MEDIA: Scene 15 (Experiment).MOV: 00:42-00:54

2.11. After connecting the quartz tube to the pumping system, first evacuate the system using the primary pump**.** Then, activate the turbomolecular pump and continue pumping until a high vacuum of 5×10^{-7} millibar is achieved **[1].**

2.11.1. LAB MEDIA: Scene 16 (Experiment).MOV: 00:33-01:03

2.12. Ramp the furnace temperature to 400 degrees Celsius over 30 minutes and hold for 4 hours **[1].** Then, switch off the tubular furnace and allow the sample to cool naturally to room temperature. After cooling, unload the sample from the furnace **[2].**

2.12.1. LAB MEDIA: Scene 17 (Experiment).MOV

2.12.2. LAB MEDIA: Scene 19 (Experiment).MOV: 00:45-00:52, 01:25-01:31

3. Post-treatment of the Prepared SiCL

3.1. Lift the lower plate to gradually increase the force until the applied pressure reaches approximately 2 kilonewtons **[1].** Then, release the applied pressure **[2].**

3.1.1. LAB MEDIA: Scene 22 (Experiment).mp4**:** 00:00 – 00:05

3.1.2. LAB MEDIA: Scene 24 (Experiment).mp4**:** 00:02 – 00:05

3.2. Place the cleaned sample onto the lower electrode inside the reactive ion etching system **[1].** Pump down the chamber until a base pressure of 5×10^{-7} millibar is reached **[2].**

3.2.1. LAB MEDIA: Scene 25 (Experiment).MOV**:** 00:00 – 00:22

3.2.2. LAB MEDIA: Scene 25 (Experiment).MOV**:** 00:27 – 00:37

3.3. Once the etching process is complete, turn off both the inductively coupled plasma and radiofrequency power supplies to stop the plasma **[1].** Evacuate any remaining process gases from the chamber**.** Then, slowly vent the chamber back to atmospheric pressure **[2].**

3.3.1. LAB MEDIA: Scene 27 (Experiment).MOV: 00:24 – 00:31

3.3.2. LAB MEDIA: Scene 27 (Experiment).MOV: 02:47 – 02:58

3.4. Finally, remove the etched sample from the chamber **[1].**

3.4.1. LAB MEDIA: Scene 27 (Experiment).MOV**:** 03:35-03:47

Results

4. Results

4.1. The X-ray diffraction pattern confirmed the formation of the type II Silicon clathrate phase in both the pressed and pressed-etched samples, with sharp peaks matching the ICDD 01-089-5534 *(I-C-D-D-zero-One-Zero-Eight-Nine-Five-Five-Three-Four)* **[1],** and weak reflections indicating the presence of a minor type 1 silicon clathrate secondary phase **[2].** After etching, the peak positions remained unchanged but showed a slight reduction in intensity **[3].**

4.1.1. LAB MEDIA: Figure 3. *Video editor: Highlight the peaks in both the "Pressed sample" and "Pressed-etched sample" .*

4.1.2. LAB MEDIA: Figure 3. *Video editor: Highlight the small peaks in both patterns that align with the blue Na8Si46 markers.*

4.1.3. LAB MEDIA: Figure 3. *Video editor: Compare the peak heights of the "Pressed-etched sample" to those of the "Pressed sample"*

4.2. Raman spectroscopy revealed that both pressed and pressed-etched samples exhibited characteristic peaks near 185, 290, and 460 inverse centimeters**,** corresponding to the Si20 *(S-I-Twenty)* and Si28 *(S-I-Twenty-Eight)* cages in the type II clathrate structure **[1].**

4.2.1. LAB MEDIA: Figure 4. *Video editor: Highlight the Raman peaks labeled Eg, T2g, and A1g in both sample curves.*

4.3. Photoluminescence measurements showed a broad emission band centered around 1.75 electron volts in both pressed and pressed-etched samples, consistent with the quasi-direct band gap of semiconducting silicon clathrates **[1].**

4.3.1. LAB MEDIA: Figure 5.

4.4. SEM *(S-E-M)* top-view images of the pressed sample revealed a smoother surface with significantly reduced grain boundaries **[1],** while cross-sectional views showed improved film density and structural connectivity **[2].**

4.4.1. LAB MEDIA: Figure 6. *Video editor: Highlight 6A*.

4.4.2. LAB MEDIA: Figure 6. *Video editor: Highlight 6B*

4.5. After SF6 dry etching, SEM top-view images showed a transformation to a textured surface morphology **[1],** and cross-sectional images confirmed changes in surface

structure compared to the unetched film **[2].**

4.5.1. LAB MEDIA: Figure 6. *Video editor: Highlight 6C*

4.5.2. LAB MEDIA: Figure 6. *Video editor: Highlight 6D*

1. **substrate**
   Pronunciation link: https://www.merriam-webster.com/dictionary/substrate
   IPA: /ˈsʌbˌstreɪt/
   Phonetic Spelling: SUB-strate
2. **hydrofluoric** (as in hydrofluoric acid)
   Pronunciation link: https://www.merriam-webster.com/dictionary/hydrofluoric
   IPA: /ˌhaɪdroʊflʊˈɒrɪk/
   Phonetic Spelling: hy-droh-flu-OR-ik
3. **cyclohexane**
   Pronunciation link: https://www.merriam-webster.com/dictionary/cyclohexane
   IPA: /ˌsaɪkloʊˈhɛkˌseɪn/
   Phonetic Spelling: SY-kloh-HEK-sane
4. **Inconel**
   Pronunciation link: https://www.howtopronounce.com/inconel (How To Pronounce)
   IPA: /ɪŋkəˈnɛl/
   Phonetic Spelling: in-kuh-NEL
5. **tantalum**
   Pronunciation link: https://www.merriam-webster.com/dictionary/tantalum
   IPA: /ˈtæntələm/
   Phonetic Spelling: TAN-tuh-lum
6. **argon**
   Pronunciation link: https://www.merriam-webster.com/dictionary/argon
   IPA: /ˈɑːrgɑn/
   Phonetic Spelling: AR-gon
7. **ramp rate**
   - **ramp**: /ræmp/ (RAMP)

- **rate**: /reɪt/ (RATE)
  Full term phonetic: RAMP-rate
  (No single dictionary entry for “ramp rate” as a combined term)

8. **millibar**
   Pronunciation link: https://www.merriam-webster.com/dictionary/millibar
   IPA: /ˈmɪlibɑr/
   Phonetic Spelling: MIL-ee-bar
9. **clathrate**
   Pronunciation link: https://www.howtopronounce.com/clathrate (How To Pronounce)
   IPA: /ˈklæθˌreɪt/
   Phonetic Spelling: KLATH-rate
10. **photoluminescence**
    Pronunciation link: https://www.merriam-webster.com/dictionary/photoluminescence
    IPA: /ˌfoʊtoʊˌluːməˈnɛsəns/
    Phonetic Spelling: FOH-toh-loo-muh-NES-ens
11. **inverse centimeters** (as in “inverse centimeters”)
    – **inverse**: https://www.merriam-webster.com/dictionary/inverse
    IPA: /ɪnˈvɜrs/
    Phonetic Spelling: in-VURS
    – **centimeter**: https://www.merriam-webster.com/dictionary/centimeter
    IPA: /ˈsɛntɪˌmitər/
    Phonetic Spelling: SEN-tuh-mee-ter
    Combined: in-VURS SEN-tuh-mee-terz
12. **inductively coupled plasma (ICP)**
    – **inductively**: https://www.merriam-webster.com/dictionary/inductive
    IPA: /ɪnˈdʌktɪvli/
    Phonetic Spelling: in-DUK-tiv-lee
    – **coupled**: /ˈkʌpəld/
    Phonetic Spelling: KUP-uhld
    – **plasma**: https://www.merriam-webster.com/dictionary/plasma
    IPA: /ˈplæzmə/
    Phonetic Spelling: PLAZ-muh