

Remote Electrochemical Epitaxy

Li-Yu Tang¹, Ching-Tai Fu², Po-Chun Hsu^{3*}

¹Department of Materials Science and Engineering, NCKU, Tainan, Taiwan

²Pritzker School of Molecular Engineering, University of Chicago

³Assistant Professor, Pritzker School of Molecular Engineering, University of Chicago

*E-mail : pochunhsu@uchicago.edu

Advanced heterogeneous integration technologies are essential for next-generation electronics, but a key challenge remains in the production and integration of single-crystalline materials. This study focuses on remote electrochemical epitaxy for the growth of high-quality, single-crystal Cu₂O thin films with defined in-plane and out-of-plane registry. Combining electrochemical epitaxy and two-dimensional (2D) materials, we demonstrate epitaxial growth of Cu₂O(111) on Au(111)/Si(111) substrates through a monolayer graphene. The results highlight the potential of remote epitaxy for integrating single-crystalline materials into next-generation electronic devices.

Introduction—Advanced heterogeneous integration technologies play a pivotal role in the development of next-generation electronics, yet one of the key challenges lies in the scalable production and integration of high-quality, single-crystalline materials. In this study, we explore the potential of remote epitaxy combined with electrochemical epitaxy to address this issue by growing single-crystalline Cu₂O thin films on Au(111)/Si(111) substrates through monolayer graphene.

Our research demonstrates a simple and cost-effective liquid-phase electrochemical epitaxy process to grow Cu₂O thin films with defined in-plane and out-of-plane registry. This technique not only produces high-quality single-crystalline materials effectively but also exhibits great flexibility for material integration owing to remote epitaxy. By leveraging this method, we aim to advance semiconductor technologies, with applications extending to solar fuels, photovoltaics, transistors, detectors and photoelectrochemical (PEC) devices.¹⁻⁴ In

this report, we present our electrochemical growth process, the dry transfer of single-layer graphene enabling remote epitaxy, and single-crystal Cu₂O thin film characterization via scanning electron microscopy (SEM), X-ray diffraction (XRD), and X-ray pole figure. Our findings confirm the successful growth of single-crystalline Cu₂O films with promising potential for transferring and integrating semiconductor epilayers, attributed to the reusability of graphene-coated substrates.

Epitaxy in Technology—Epitaxy, derived from the Greek words "epi" (meaning "above") and "taxis" (meaning "in ordered manner"), refers to the deposition of an overlayer on a crystalline substrate, ensuring that the overlayer is aligned with the substrate. This process allows for the growth of high-quality, nearly defect-free materials, which are crucial for applications such as semiconductors and LEDs. A notable example is the 2014 Nobel Prize in Physics, awarded for the development of blue LEDs,

which utilized epitaxy to create high-quality gallium nitride (GaN) layers.⁵

Epitaxy is widely applied in semiconductor technology, with vapor-phase epitaxy (VPE) and liquid-phase epitaxy (LPE) being the two most-common techniques. The key difference between these methods lies in the state of the source material used to form epilayers. VPE can be divided into physical, chemical, or molecular beam epitaxy (MBE), the latter being the most prevalent in the semiconductor industry. MBE deposits high-quality single crystals which demand high vacuum levels, high temperatures and sophisticated instruments.⁶ However, compared to MBE, LPE – electrochemical epitaxy in particular – offers several key advantages. LPE is more cost-effective due to simpler instrumentation, and its ability to operate at room temperature and ambient pressure consequently provides a higher growth rate, making it more suitable for large-scale production.

Cu₂O and Remote Epitaxy—Copper oxide (Cu₂O) is a direct bandgap semiconductor with a bandgap ranging from 1.9 to 2.2 eV, enabling it to absorb visible light and generate electron-hole pairs for driving PEC reactions. Its strong photoelectric properties make it a favored material for applications such as photoelectrodes.⁷⁻⁸

In my previous work with Professor Wen Hui Cheng at NCKU, we identified a potential connection between Cu₂O and CO₂ reduction. By measuring the CO₂ reduction rate of the Cu₂O (111) plane and comparing it with other planes like (110) and (100), we aim to elucidate how various crystal orientations affect the performance of PEC devices.

Remote epitaxy, a technique where single-crystalline thin films are grown on 2D-material-coated substrates, has enabled new conceptual understanding for developing novel single-crystal Cu₂O thin film devices. Due to weak adhesion at the 2D interface, epilayers can be precisely exfoliated, releasing a pristine, smooth and reusable underlying graphene-coated substrate. Given the low lattice mismatch of 1.8% between Au and Cu₂O, remote epitaxy provides a scalable, efficient and cost-effective method for fabricating beyond state-of-the-art Cu₂O PEC devices.⁹⁻¹²

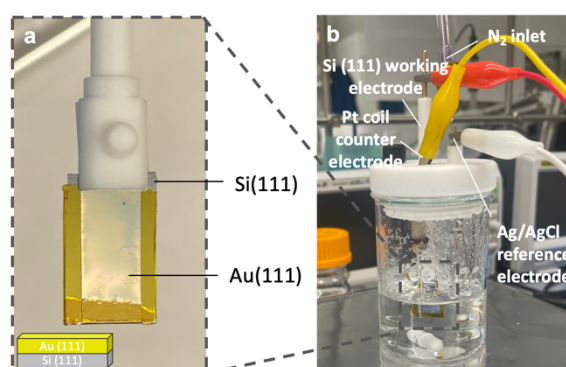


Figure 1. Electrochemical epitaxy setup for Au(111) thin films. (a) Si(111) working electrode. (b) Three-electrode configuration for electrochemical epitaxial growth of Au(111) thin films.

Methods—In the first step, a single-crystal Au(111) buffer layer is grown on top of a Si(111) wafer with resistivity between 0.001-0.005 Ω cm (MTI Corp.). Single-crystal Cu₂O(111) was electrodeposited with Au(111)/Si(111) as the working electrode, Ag/AgCl as the reference electrode, and a Pt coil serving as the counter electrode (Figure 1b). The single-crystal gold buffer layer grown on the Si substrate is depicted in Figure 1a. Next, monolayer graphene, a 2D material, was dry transferred onto the gold surface for remote epitaxy. The graphene

used was CVD-grown on copper foil, and exfoliation was achieved using a nickel stressor layer and thermal release tape. After exfoliating the graphene, the nickel stressor was heat pressed onto the gold-coated silicon substrate at 130°C for 2 minutes, allowing for the easy removal of the thermal release tape. Nickel was then etched away using ferric chloride and hydrochloric acid, leaving the monolayer graphene successfully transferred onto the gold, as shown in Figure 2.

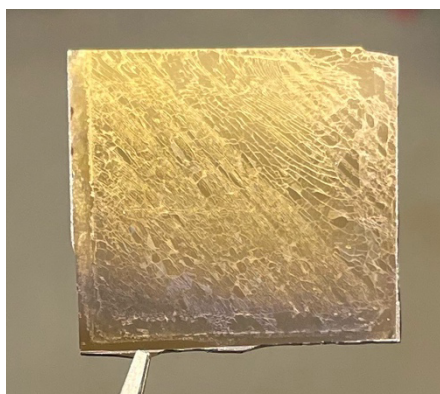


Figure 2. Monolayer Graphene on Gold.

Single-crystalline copper oxide (Cu_2O) was deposited on Graphene/Au(111)/Si(111) under chronopotentiometry (CP) using a two-electrode configuration, with Pt as the counter electrode. This setup, as shown on Figure 3b, facilitated the growth of high-quality single-crystal Cu_2O on the graphene-coated gold substrate, Figure 3a.

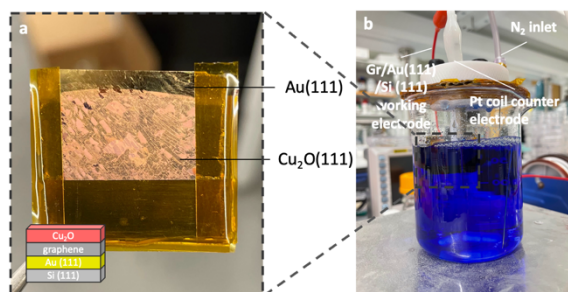


Figure 3. Electrochemical epitaxial growth setup for copper oxide.

(a) $\text{Cu}_2\text{O}(111)$ /Graphene/Au(111)/Si(111) working electrode. (b) Two-electrode

configuration for electrochemical epitaxial growth of Cu_2O (111) thin films.

Results—In this study, materials characterization was conducted using Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD), and X-ray pole figure to analyze the morphology, out-of-plane and in-plane crystal orientation of electrochemically grown Cu_2O thin films, respectively.

SEM Analysis—When observing the SEM image shown on Figure 4, we can see smooth areas along with some small particles. Thus, we can infer that our epitaxial layer has undergone the process of coalesced film growth. The smooth areas indicate that most of the Cu_2O particles have merged to form a continuous film structure. In contrast, the small particles may represent portions that have not fully fused during the coalescence process.

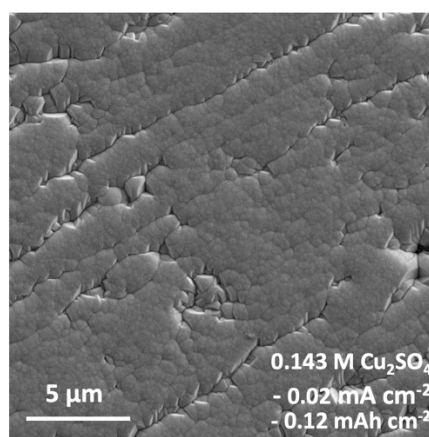


Figure 4. SEM figure of copper oxide electrochemical epitaxial layers on Graphene/Au(111)/Si(111).

XRD Analysis—Figure 5 presents the XRD pattern, which confirms the successful deposition of both Cu_2O and Au on the Si substrate. The diffraction peaks allow us to extract out-of-plane information, confirming the preferred (111) orientation of the Cu_2O . To further verify that the Cu_2O film is

oriented in-plane, pole figure analysis was performed.

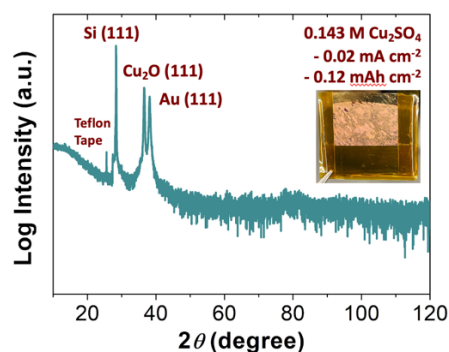


Figure 5. XRD pattern of $\text{Cu}_2\text{O}(111)/\text{Graphene}/\text{Au}(111)/\text{Si}(111)$ electrochemical epitaxial layers.

Pole Figure Analysis—Pole figure analysis was performed to examine the crystal's in-plane registry. In this method, the sample is tilted $0\text{--}90^\circ$ (χ) and rotated $0\text{--}360^\circ$ (φ) to detect specified planes at the defined 2θ . Planes with d-spacing corresponding to the Bragg angle yield an intensity map as a function of tilt and rotation.

Figure 6a shows the pole figure for $\text{Si}(220)$, revealing three distinct spots that correspond to the three-fold symmetry of the silicon substrate. Figure 6b demonstrates that the Au buffer layer on Si exhibits two sets of three-fold symmetry, which we attribute to twin boundaries in the gold layer. Gold, with a face-centered cubic (FCC) structure and its densely packed and low-energy (111) plane, facilitates the formation of twin boundaries, which means two crystal regions having a mirror-image orientation. As shown in the cubic model next to Figure 6b, if a twin boundary forms, the (111) plane rotates 60° , producing two sets of three-fold symmetry. Figure 6c shows the (220) pole figure of Cu_2O , exhibiting a three-fold symmetry. As we look closely, we can determine that there are two sets of poles in

Fig. 6c: two sets of three-fold symmetry on the outer ring, and one set of three-fold symmetry on the inner ring, corresponding to $\text{Au}(220)$ and $\text{Cu}_2\text{O}(220)$, respectively. $\text{Au}(220)$ and $\text{Cu}_2\text{O}(220)$ have very similar Bragg angles, so we speculate that this is why Fig. 6c shows two sets of poles on the same plot.

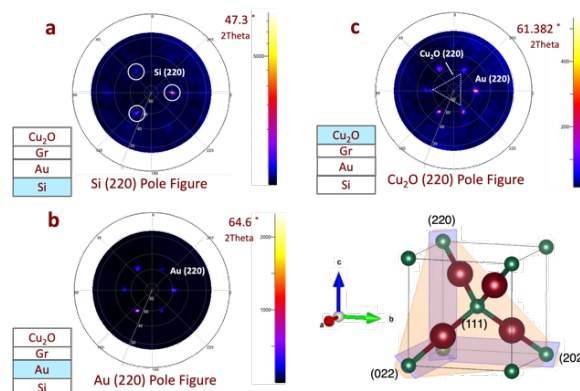


Figure 6. X-ray pole figure of $\text{Cu}_2\text{O}(111)/\text{Graphene}/\text{Au}(111)/\text{Si}(111)$. (a) Pole figure of $\text{Si}(220)$ orientation. (b) Pole figure of $\text{Au}(220)$ orientation. (c) Pole figure of $\text{Cu}_2\text{O}(220)$ orientation.

From another perspective, we know the excellent lattice matching between Au and Cu_2O , with only 1.8% lattice mismatch. As shown on Fig. 7, we can observe that Au and Cu_2O are almost perfectly matched. Hence, the $\text{Cu}_2\text{O}(111)$ epilayer grows along the $\text{Au}(111)$ epilayer instead of the underlying silicon(111) substrate.

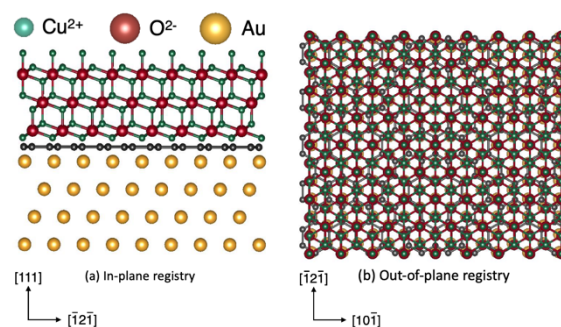


Figure 7. Schematic crystal structure of $\text{Cu}_2\text{O}(111)/\text{Graphene}/\text{Au}(111)/\text{Si}(111)$. (a) In-plane registry. (b) Out-of-plane registry.

Despite the presence of twin boundaries in the gold layer, the sample maintains a continuous crystal lattice, confirming that both the Cu₂O and gold layers still qualify as single crystals.

Conclusions and Future Works—In this study, we successfully confirmed the growth of single-crystalline Cu₂O thin films through X-ray diffraction (XRD) and pole figure analysis. A key finding is that proper temperature control and the application of heat significantly improve the performance of graphene transfer, which plays a critical role in the success of the remote epitaxy process.

Future work will focus on exfoliating the Cu₂O layer and transferring it to different substrates while reusing the Au(111)/Si(111) substrate for additional Cu₂O growth. Further research will also explore the PEC performance of Cu₂O with different crystallographic orientations in collaboration with NCKU.

Acknowledgements— I would like to express my sincere gratitude to Professor Po-Chun Hsu and Professor Wen Hui Cheng at NCKU for their guidance and support throughout this project. A special thank you to Professor Chin and everyone involved in arranging this program. I am incredibly grateful for the opportunity to conduct research at the University of Chicago. I also want to extend my heartfelt thanks to Hsu group for helping me settle into the lab, particularly my mentor Vincent, as well as Ron and Han Yu for their continuous support and assistance.

[1] Pan, L., Dai, L., Burton, O.J. *et al.* High carrier mobility along the [111] orientation

in Cu₂O photoelectrodes. *Nature* **628**, 765–770 (2024). <https://doi.org/10.1038/s41586-024-07273-8>

[2] Mahenderkar, N. K., Chen, Q., Liu, Y. C. *et al.* Epitaxial lift-off of electrodeposited single-crystal gold foils for flexible electronics. *Science*, 1203–1206(2017). <https://doi.org/10.1126/science.aam5830>

[3] Zheng, J., Zhao, Q., Tang, T. *et al.* Reversible epitaxial electrodeposition of metals in battery anodes. *Science*, 645–648(2019). <https://doi.org/10.1126/science.aax6873>

[4] Roh, I., Goh, S. H., Meng, Y. *et al.* Applications of remote epitaxy and van der Waals epitaxy. *Nano convergence*, 10(1), 20(2023). <https://doi.org/10.1186/s40580-023-00369-3>

[5] Von Dollen, P., Pimputkar, S., & Speck, J. S. Let there be light—with gallium nitride: the 2014 Nobel Prize in Physics. *Angewandte Chemie (International ed. in English)*, 53(51), 13978–13980 (2014). <https://doi.org/10.1002/anie.201410693>

[6] John R. Arthur. Molecular beam epitaxy. *Surface Science*, Volume 500, 189–217(2002). [https://doi.org/10.1016/S0039-6028\(01\)01525-4](https://doi.org/10.1016/S0039-6028(01)01525-4).

[7] René Wick, S. David Tilley. Photovoltaic and Photoelectrochemical Solar Energy Conversion with Cu₂O. *J. Phys. Chem.* 119, 26243–26257(2015). DOI:10.1021/acs.jpcc.5b08397J.

[8] Indrajit V. Bagal, Nilesh R. Chodankar. *et al.* Cu₂O as an emerging photocathode for solar water splitting - A status review, *International Journal of Hydrogen Energy*,

Volume 44, 21351-21378(2019).
<https://doi.org/10.1016/j.ijhydene.2019.06.184>.

[9] Kim, Y., Cruz, S., Lee, K. *et al.* Remote epitaxy through graphene enables two-dimensional material-based layer transfer. *Nature* **544**, 340–343 (2017).
<https://doi.org/10.1038/nature22053>

[10] Kim, H., Chang, C.S., Lee, S. *et al.* Remote epitaxy. *Nat Rev Methods Primers* **2**, 40 (2022).
<https://doi.org/10.1038/s43586-022-00122-w>

[11] Xin Sun, Zonghuan Lu, Yu Xiang, Yiping Wang, Jian Shi, Gwo-Ching Wang, Morris A. Washington, and Toh-Ming Lu
ACS Nano **2018** *12* (6), 6100-6108
DOI: 10.1021/acsnano.8b02374

[12] Bo-In Park, Jekyung Kim, Kuangye Lu, Xinyuan Zhang, Sangho Lee, Jun Min Suh, Dong-Hwan Kim, Hyunseok Kim, and Jeehwan Kim
Nano Letters **2024** *24* (10), 2939-2952
DOI: 10.1021/acs.nanolett.3c04465