Structure and Properties of $Cu(InGa)Se_2$ nanowires

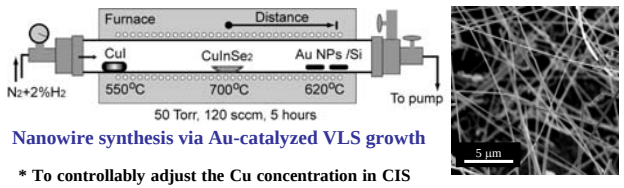
Hailin Peng, David T. Schoen, Chong Xie, Stefan Meister, Yi Cui*

Department of Materials Science and Engineering, Stanford University, Stanford, CA 94305, Email: hlpeng@stanford.edu

MOTIVATION

Polycrystalline $CuInSe_2$ (CIS) and $Cu(InGa)Se_2$ (CIGS) solar cells have the highest conversion efficiency (~20%) among all the thin-film solar cell technologies. CIS is commonly paired with CdS to form the p-n heterojunction that separates the photogenerated electron-hole pairs. Important issues on the microstructure and formation mechanism of CIS-CdS p-n heterojunction persist due to the complexity of polycrystalline films and invasive sample preparation for characterization. Here we exploited a Au-catalyzed VLS growth for single crystalline p- and n-type CIS (CIGS) NWs. The p-CIS/n-CdS core/shell NW epitaxial heterostructures as solar cell devices were fabricated by CdS CBD process. We investigated the microstructure, chemical composition and formation mechanism of the junction with CIS-CdS core-shell nanowires, where nanowire geometry affords single-crystalline nanograins for direct characterization. Our results provide important understanding of CIS-CdS heterojunctions for developing better CIS solar cells.

SYNTHESIS OF NANOWIRES

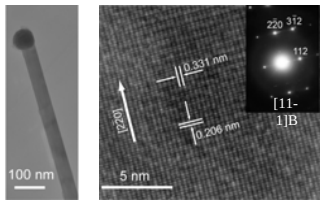


Nanowire synthesis via Au-catalyzed VLS growth

CIS nanowires

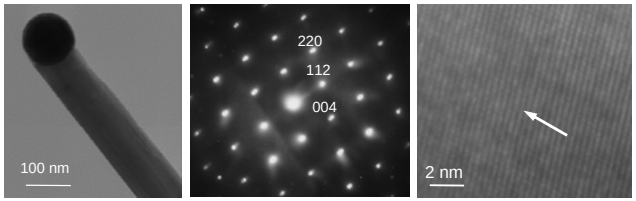
*** To controllably adjust the Cu concentration in CIS NWs, additional CuI powder was placed upstream.**

STRUCTURE OF NANOWIRES



TEM images and SAED pattern of Cu-rich CIS NW

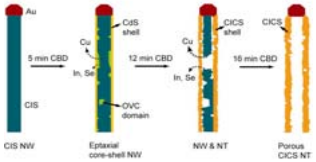
EDX data of Cu-rich CIS NW



TEM images and SAED pattern of CIGS NW

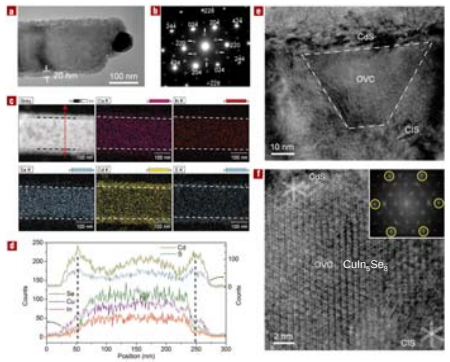
CORE-SHELL NANOWIRE & NANOTUBE

❖ Formation process of CIS-CdS core-shell nanowires and nanotubes through a nanoscale Kirkendall effect



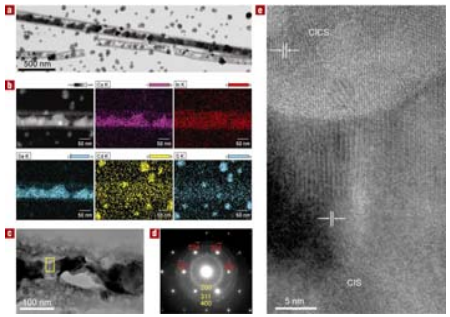
- **The single-crystalline CIS nanowires are coated with a thin CdS layer via 5 min chemical bath deposition (CBD) at 60 ºC, forming core-shell CIS-CdS epitaxial nanowires.**
- **Ordered vacancy compound (OVC) nanodomains (green) form at the CIS-CdS interface mainly due to Cu fast outward diffusion.**
- **The 12 min CBD leads to the formation of nanoscale voids by a Kirkendall effect. The shell composition becomes CICS (orange).**
- **Polycrystalline CICS nanotube forms after 16 min CBD.**

❖ CIS-CdS core-shell NW after 5 min CBD



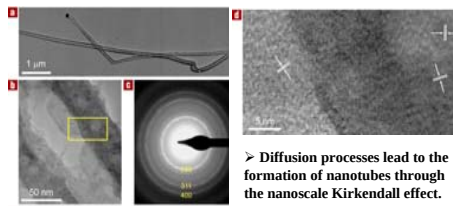
- **A coherent CdS shell can be epitaxially deposited onto the $CuInSe_2$ nanowire with CBD even at 60ºC.**
- **The EDX mapping indicates a significant outward diffusion of Cu while little diffusion of In and Se.**
- **Ordered vacancy compound (OVC) nanodomains induced by fast outward diffusion of Cu were directly observed near the interface of epitaxial CIS-CdS hetero-structure For the first time.**

❖ Formation of voids through a nanoscale Kirkendall effect after 12min CBD



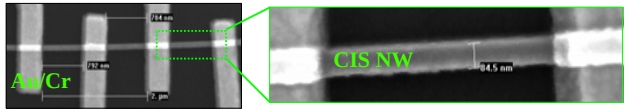
- **TEM images of nanotubes with remaining core CIS, show the random-sized Kirkendall voids distributed at the interface.**
- **EDS mapping data confirm the outward diffusion of Cu, In, and Se.**
- **HRTEM image shows remaining single-crystalline CIS grains imbedded in the polycrystalline $CuInCdSe_2S$ (CICS) shell.**

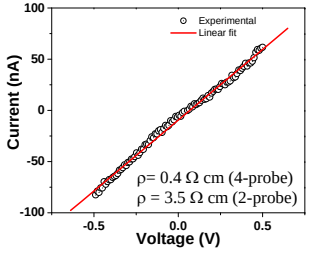
❖ Formation of nanotubes after 16 min CBD

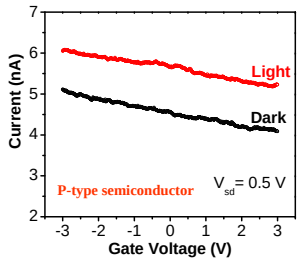


- **Diffusion processes lead to the formation of nanotubes through the nanoscale Kirkendall effect.**
- **EDX analysis indicates that the nanotubes are composed of Cu, In, Se, Cd and S. The elemental distribution is quite uniform along the tube.**
- **TEM images and SAED pattern indicate the polycrystalline nanotube.**
- **The presence of small voids and cracks in the nanotube wall.**

ELECTRICAL MEASUREMENT

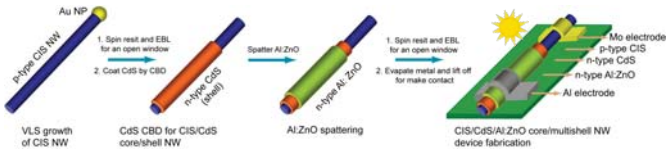




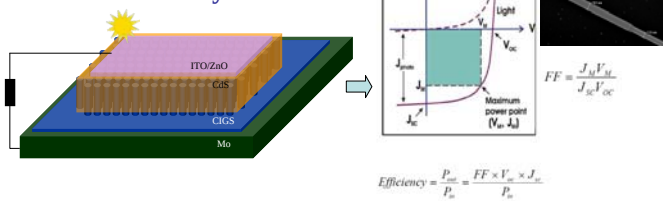


FUTHURE WORK

❑ Single nanowire solar cell



❑ Nanowire array solar cell



CONCLUSIONS

- **Single crystalline Cu-rich and Cu-deficient $Cu(InGa)Se_2$ NWs were synthesized via a Au-catalyzed VLS growth for the first time.**
- **The Cu-rich CIS NW is p-type semiconductor with resistivity of 0.4 Ω cm.**
- **A coherent CdS shell can be epitaxially deposited onto the CIS nanowire with chemical bath deposition (CBD) even at 60ºC.**
- **For the first time, ordered vacancy compound (OVC) nanodomains induced by fast outward diffusion of Cu were directly observed near the interface of epitaxial CIS-CdS heterostructure.**
- **The core-shell nanowires can be transformed into nanotubes with CBD progression through a nanoscale Kirkendall effect.**

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