Selective-Area Atomic Layer Deposition of Copper Nanostructures for Direct Electro-Optical Solar Energy Conversion

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Plasmonics

Au, Ag, Cu Nanoparticles interact strongly with visible/near IR radiation, **tunable** by size/shape.

Quasi-Static Approximation

\[ \alpha = 4\pi a^3 \frac{\varepsilon(\omega) - \varepsilon_m}{\varepsilon(\omega) + 2\varepsilon_m} \]

Resonance at Re [\(\varepsilon(\omega)\)] = -2\(\varepsilon_m\)

Plasmonic nanoparticles have applications for localized heating, SERS, nanophotonics, catalysis, sensors and more…

Van Duyne, Nat. Mater. 2008
“hot spots” are created by “plasmonic dimers”

Geometric effect concentrates electric fields at nano-gaps leading to large field enhancements.

EM field induces a voltage drop across the nanoelectrodes.
Theoretical studies predict large enhancements in rectification ratios for plasmonic resonances.

Lightning rod effect concentrates field at tip = asymmetry.
Optical Rectification

Concept: direct conversion of EM radiation (solar) into DC power by antenna – coupled high speed diodes to rectify optical frequency charge waves.

Potential Advantages: low cost fabrication, tunable absorbance including IR (waste heat), and device integration.
Ward et al have demonstrated optical rectification in an electromigration junction.

- not tuned for plasmonic resonance
- not scalable
- no control of geometry
- isolated nanostructures
Rectenna Concept

- Electrically connected
- Sized for plasmon resonance in visible
- Asymmetric geometry
- Nanoscale tunnel gap

Not commercially available!
Rectenna Challenges

Nanoscale antenna tuned to visible/near-IR

Geometric asymmetry, diode response at low voltage

Electrically contacted, tunneling devices

RC time constant, impedance matching

Extremely fast diodes, $10^{15}$ Hz

Diode is most critical need!
Rectenna Concept

- Electrically connected
- Asymmetric geometry
- Sized for plasmon resonance in visible
- Nanoscale tunnel gap

**ALD used to make tunnel diodes**
Choices for ALD Cu, Ag, and Au are limited, non-ideal.

Cu(II)thd$_2$/H$_2$ process is well-behaved for selective growth.
Selective area ALD enables deposition on seeded regions and eliminates the need for etching.

SA-ALD enables nanostructures.
Plasmonic Structures

Pd nanostructures

10x10 “Rectangular Dipole” Rectenna Array, 550 nm x 800 nm spacing

10x10 “Large Triangle” Rectenna Array 500 nm x 500 nm spacing

Electrically isolated structures are used to investigate tuning of plasmonic response by selective area ALD.
FDTD simulations predict that resonance red-shifts for decreasing gap size and for increasing nanostructure size.
Plasmonic dimers have strong electric field enhancement $>10^3$, with fields $>5\times10^8$ V/m \(^1\).

\(^1\)Ward et al., Nature Nano v. 5 p. 732 (2010)
Focus spot is 3-7 \( \mu \text{m} \); sized to the test array.
Optical Response

Spectroscopy data show red-shift after ALD.

Red-shift & increased extinction
Red-shift magnitude tracks ALD thickness/cycles.

In-situ measurements would provide feedback on nanogap.
Device arrays with 1000’s of tips converge to tunneling similarly to suspended structures.

Geometric asymmetry contributes to desired diode IV character.
ALD Grown Tunnel Junctions

Trapping and IETS detection of Acetic Acid molecules in nanojunctions
HIM provides some estimates for gap size.

Hang Dong, Rutgers
Nano-Nucleation Challenges

Growth is sensitive to surface pre-treatment, growth inhibition is observed without UVO.

ALD metal films are not layer-by-layer, Nanograins form with inherent surface roughness. How smooth can we achieve? Could be shape dependence, crystal structure effects.
UV/Ozone Sample Pre-treatment

ALD Cu roughness values are similar to other reports\(^2\), scales with thickness.

UVO enhances/enables growth, removes most C 1s, but residual C remains even after long time (60 min).

Selectivity

Selectivity is lost at higher temperatures, inverted selectivity?

Selectivity was a mystery; how does Cu grow on oxide?
Cu(thd)$_2$ is a solid source precursor. H$_2$ is co-reactant.

In-situ, real time SE provides saturation curves.
in-situ SE provides growth “finger-print”, sensitive to substrate preparation and growth conditions.

extracted GPC $\sim 0.04$ nm/cycle matches SEM data.
Martensson’s mechanism

![Chemical Reaction Diagram]

Fig. 9. Proposed reaction mechanism for the deposition of copper on pure metals.

Cu(thd)$_2$ adsorbs to saturation during precursor dose.

SrO ALD shows characteristic signature for stable precursors adsorption.

Cu ALD has opposite signature with reversible adsorption.
Martensson’s mechanism

Original Mechanism

Selectivity follows from H$_2$ dissociation requirement.

Original mechanism is NOT consistent with Cu$^1$ CVD by disproportionation at 150-200°C, and can’t explain observed GPC.

New mechanism explains SE signature and is consistent with reversible adsorption. Also explains high GPC.

Roll of Pd-H$_2$ is now more complex, strong chemisorption.
SE Growth vs. Temperature

Mechanism not sensitive to temperature. H* must be stable.

Dissociative reversible adsorption is consistent with thermodynamics if $\Delta H_{\text{ads}} \sim 34$ kcal/mol.
QCM Studies

QCM measures mass and thermal effects.

Reaction signal (at 150°C) is consistent with RTSE data, GPC \( \approx 0.04 \) nm/cycle.
Temperature and time dependence of Cu XRD and XPS signals indicate extensive Cu/Pd mixing. Lower temperatures = higher Cu/Pd ratios.

ARXPS shows evidence for Pd enrichment at surface.

Pd explains H chemisorption. What happens if the Pd runs out?
Both Pt & Pd act as seed layers, but Pd mixes more extensively with Cu.
GPC decreases as Cu/Pd becomes more Cu rich.

Cu/Pd ratio measured as 45:1 for this sample.
Selectivity is evident from in-situ SE data, but how to explain non-selective growth on SiO$_2$?
Non-Selective Growth Mechanism?

C 1s signal is removed by sputtering, but O 1s signal remains. Cu 2p signal could be Cu$^0$ or Cu$^1$. Cu/O ratios are ~1.3. AES peaks indicates Cu$^1$.

CuO/Cu$_2$O growth explains non-selective growth mechanism. Mechanism requires self-decomposition. H$_2$ not required, but may affect thickness.

ราว For thick Cu films, self-decomposition may contribute to growth.
H$_2$ effect on Non-selective Growth

H$_2$ pressure plays a significant role for non-selective growth. Why?
H$_2$ effect on Non-Selective Growth

180 C
3 torr H$_2$

180 C
1.5 torr H2

180 C
0.5 torr H2
Cu ALD on Pd Seed Layers

GPC Measured by QCM in selective window shows no effect of H₂ partial pressure.

No growth without H₂.
Summary

ALD Cu is useful for tuning the optical response of plasmonic materials. ALD of Ag, Au would be nice.

Selective Area Cu ALD works well and is useful for tunnel junctions with many potential applications.

Cu ALD mechanism is partially understood, Pd, H effects are important.
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