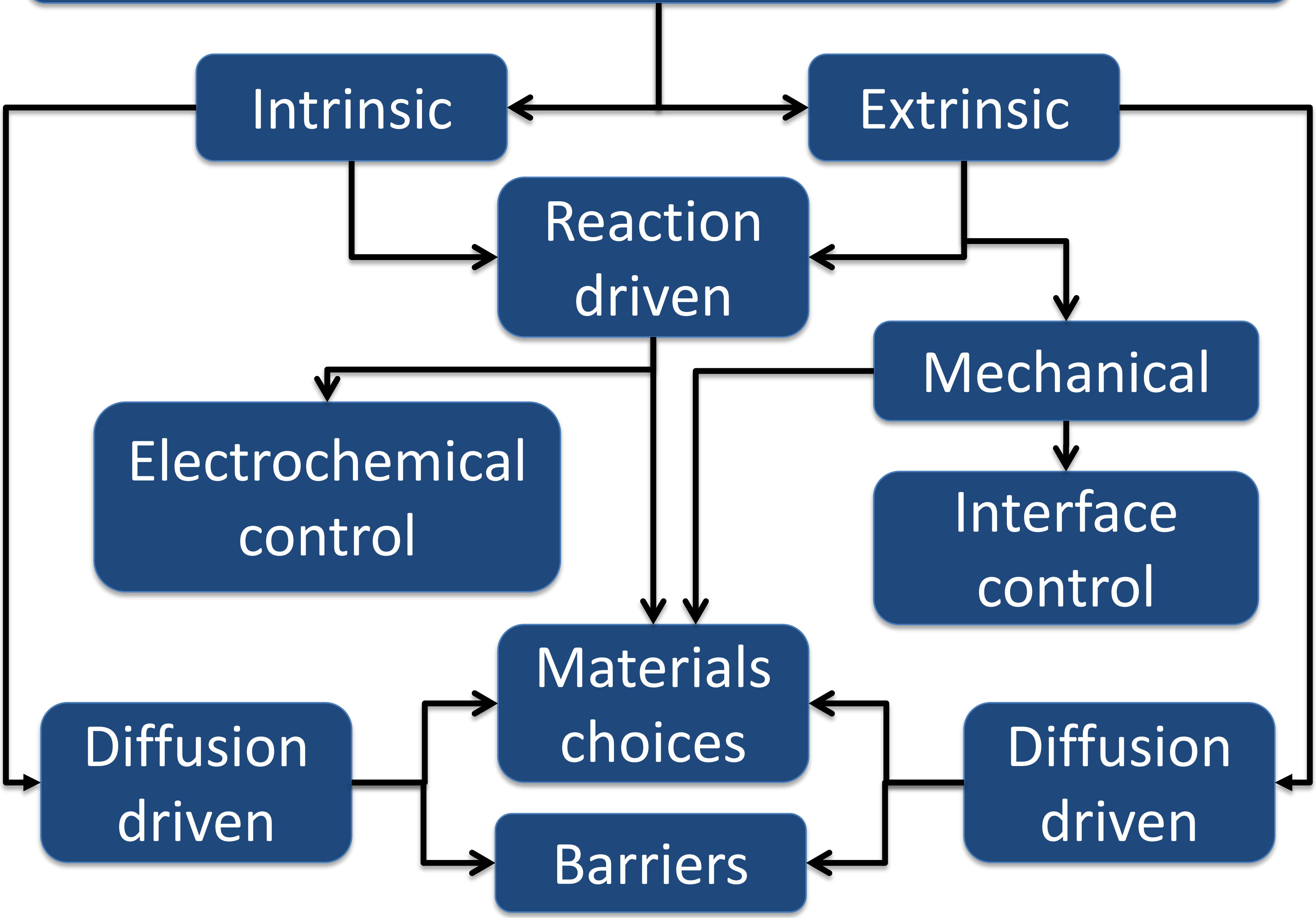
Intrinsic Chemical Instability and Metastability in Photovoltaic Devices

Angus Rockett
Department of Materials Science and Engineering, University of Illinois
1304 W. Green St., Urbana, IL 61801
arockett@illinois.edu

Module Failure Control Strategies



Intrinsic

Extrinsic

Reaction driven

Mechanical

Electrochemical control

Interface control

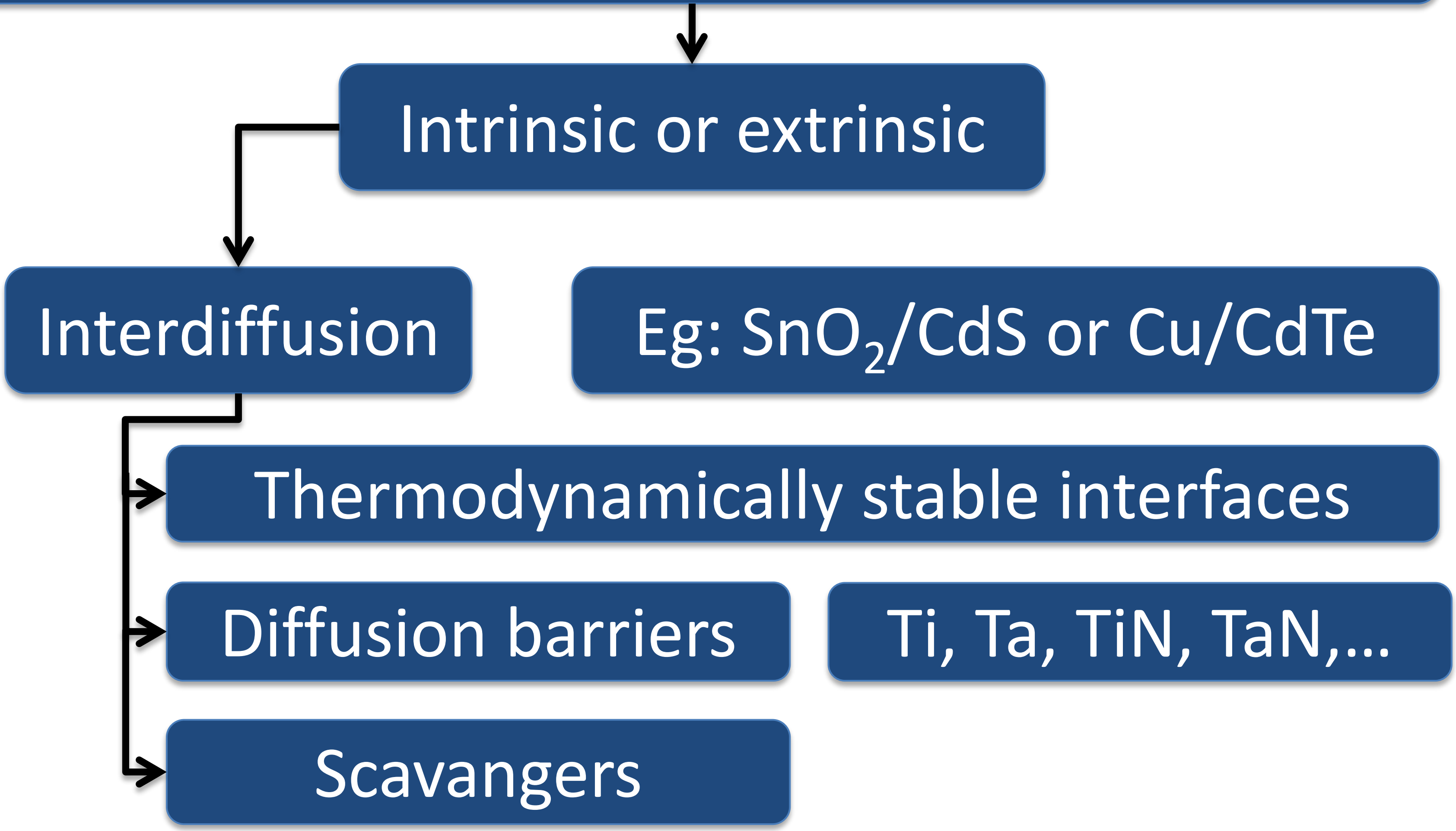
Materials choices

Diffusion driven

Diffusion driven

Barriers

Module Failure Control Strategies



Intrinsic or extrinsic

Interdiffusion

Eg: SnO_2/CdS or Cu/CdTe

- Thermodynamically stable interfaces
- Diffusion barriers
- Scavangers

Ti, Ta, TiN, TaN,…

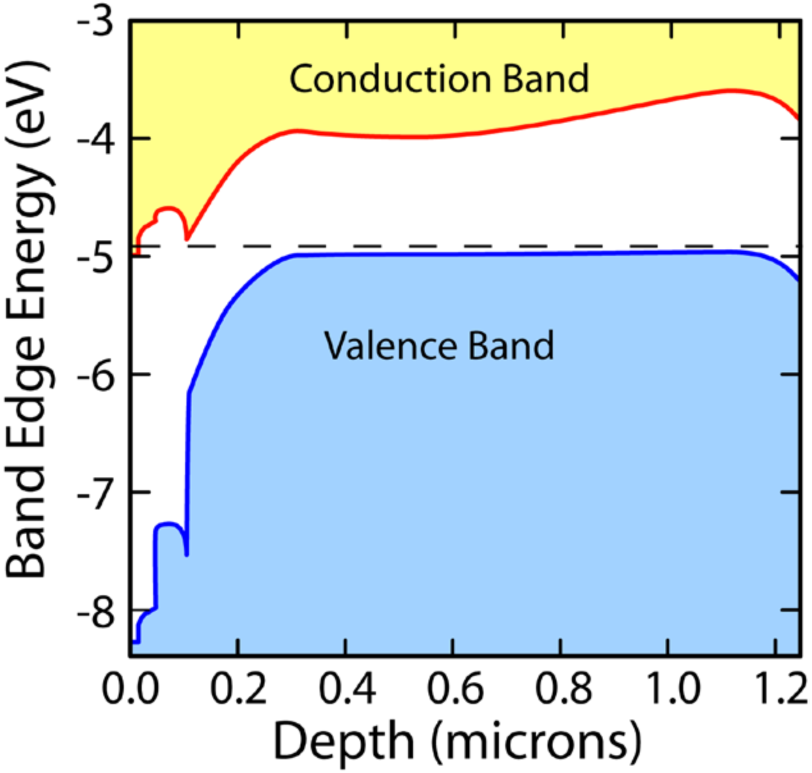
Require: 100% dense, conformal, chemically unreactive, electrically acceptable

Driven diffusion

There is a large electric field in the depletion region, which changes with forward bias. This leads to expectation of instability during operation.

May result in metastable changes in defect concentrations.

Could drive back-contact impurity diffusion in CdTe devices over time too.



Driven diffusion

Some diffusing species are charged and can respond to electric fields.

Theory shows that field driven diffusivity only increases by a factor of two. However vacancy formation energy is often chemical-potential driven. This can result in orders of magnitude changes in diffusion rates.

Vacancy formation enthalpy changes linearly with Fermi energy. Vacancy concentration changes exponentially with formation enthalpy so Fermi energy is pinned by vacancy formation.

$$\Delta E_d(q, E_f) = \Delta E_0(q) - q\Delta E_f$$

Driven diffusion

Fermi level pinning defines which defects would change near the junction.

CdTe and CIGS are both intrinsically p-type and are hard to dope n-type. Therefore when the Fermi energy rises (for example near the junction) we can expect formation of extra cation vacancies.

$$D_{impurity} = D_{q=0} + \sum_{q\leq -1} D_{-q}\left(\frac{n}{n_i}\right)^{-q} + \sum_{q\geq 1} D_{+q}\left(\frac{p}{n_i}\right)^{q}$$

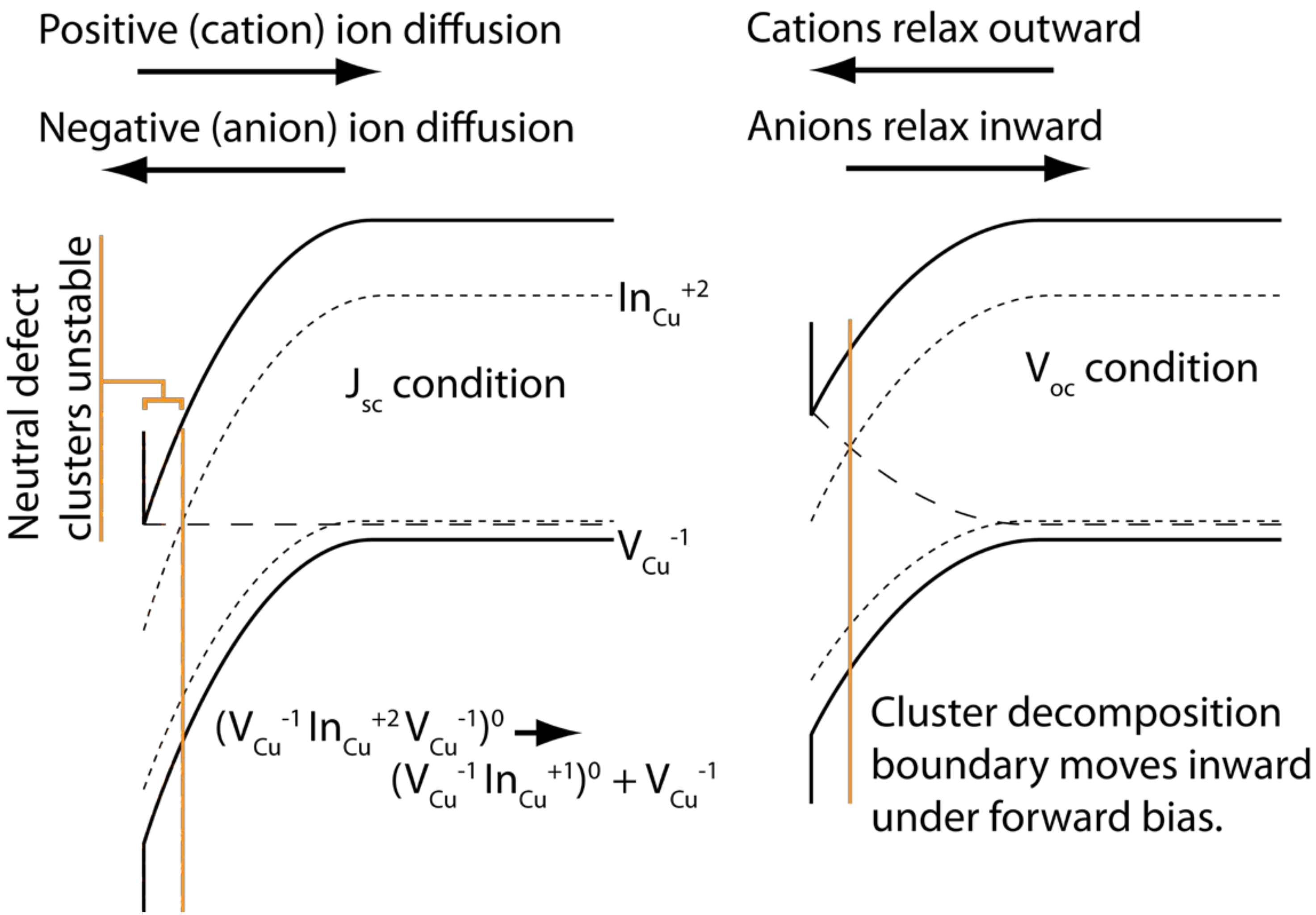
Diffusivity of species diffusing by cation vacancies (presumably the cations in the ionic material) would be expected to increase rapidly near the junction.

The vacancy gradient can drive diffusion more effectively than the field. This may be the most important factor for Cu diffusion in CdTe.

Kinetics probably limits diffusion in CIGS modules.

Metastability in CIGS Devices

Consider the electric field around the CIGS device junction:



Positive (cation) ion diffusion →

Negative (anion) ion diffusion ←

Cations relax outward ←

Anions relax inward →

Neutral defect clusters unstable

J_{sc} condition

V_{oc} condition

$(V_{Cu}^{-1} In_{Cu}^{+2} V_{Cu}^{-1})^0 \rightarrow (V_{Cu}^{-1} In_{Cu}^{+1})^0 + V_{Cu}^{-1}$

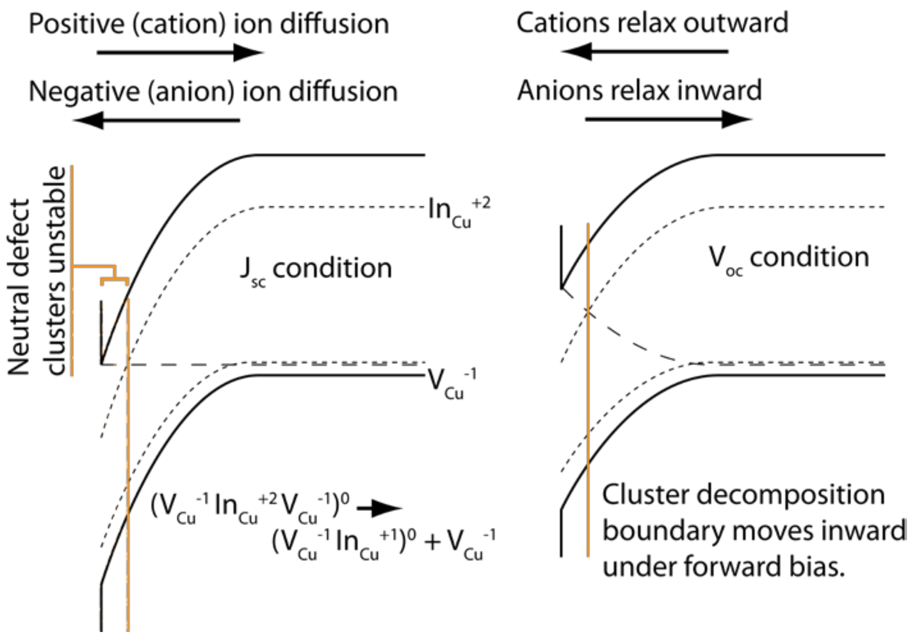
Cluster decomposition boundary moves inward under forward bias.

Possible moving species: Na^+ (grain boundaries only), vacancies (probably Cu)

Metastability in CIGS Devices

The neutral defect cluster is unstable in n-type material and can release a large number of Cu vacancies. This could significantly alter atomic mobility.

Of course at <100°C it is unlikely that the system is in equilibrium. Kinetics for long-range (nm) atomic transport seems likely too slow to explain metastability data.

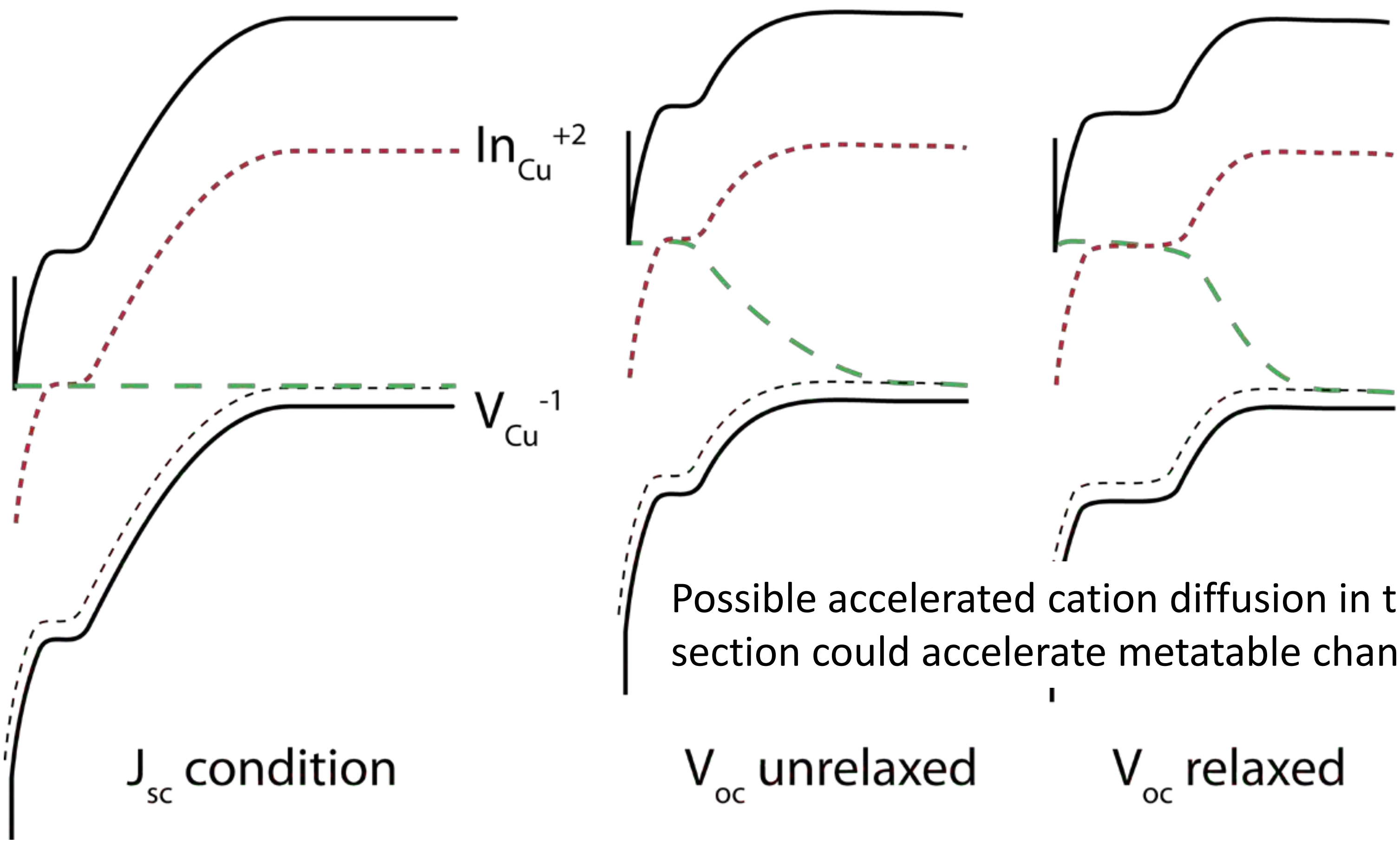


Large numbers of defects can pin the Fermi level (at least over a range of depths). This may account for the metastable behavior.

Metastability in CIGS Devices

An example of metastable changes in a device due to forward bias, not requiring long range atomic transport.

$$(V_{Cu}^{-1}\,In_{Cu}^{+2}\,V_{Cu}^{-1})^0 \rightarrow (V_{Cu}^{-1}\,In_{Cu}^{+1})^0 + V_{Cu}^{-1}$$



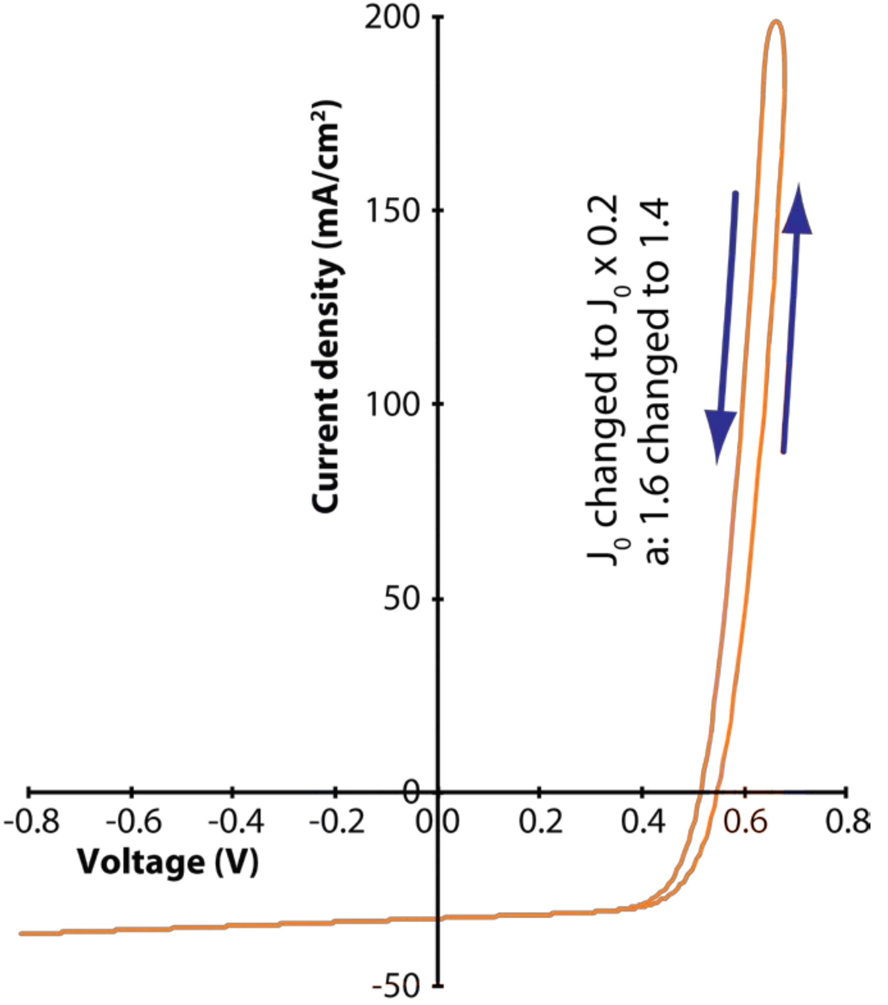
Possible accelerated cation diffusion in the outer section could accelerate metatable changes in behavior.

Short term metastability

j/V measurements (for example in CIGS cells) can show hysteresis, typically with sweep up showing a larger ideality factor and dark current.

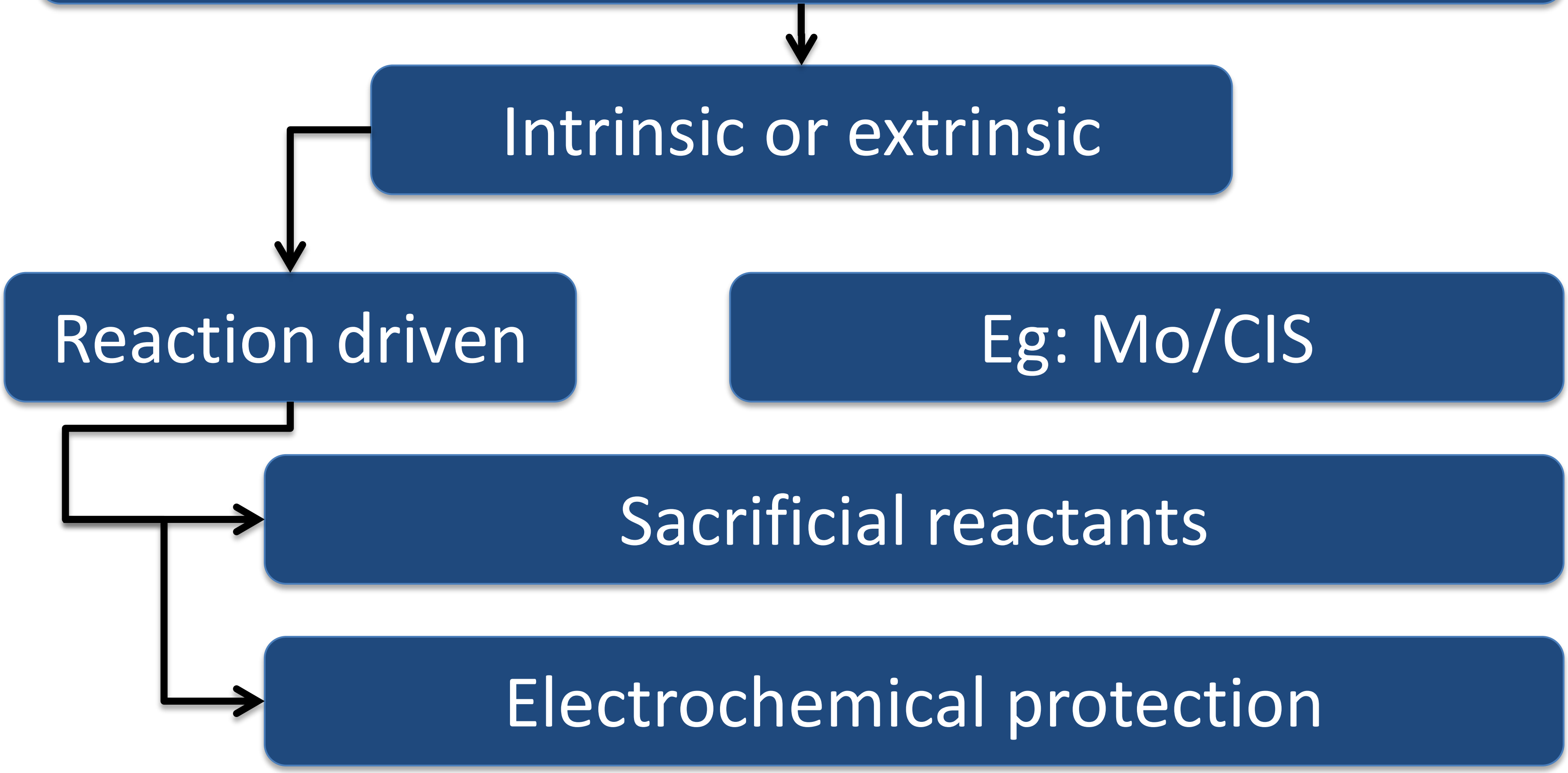
This represents metastable filling of trap states in the base by emitter injection current. **There is no atomic motion in this case.**

Sweep frequency can give information on trap depth based on the magnitude of hysterisis vs. sweep frequency.



Simulated metastable response

Module Failure Control Strategies



Intrinsic or extrinsic

Reaction driven

Eg: Mo/CIS

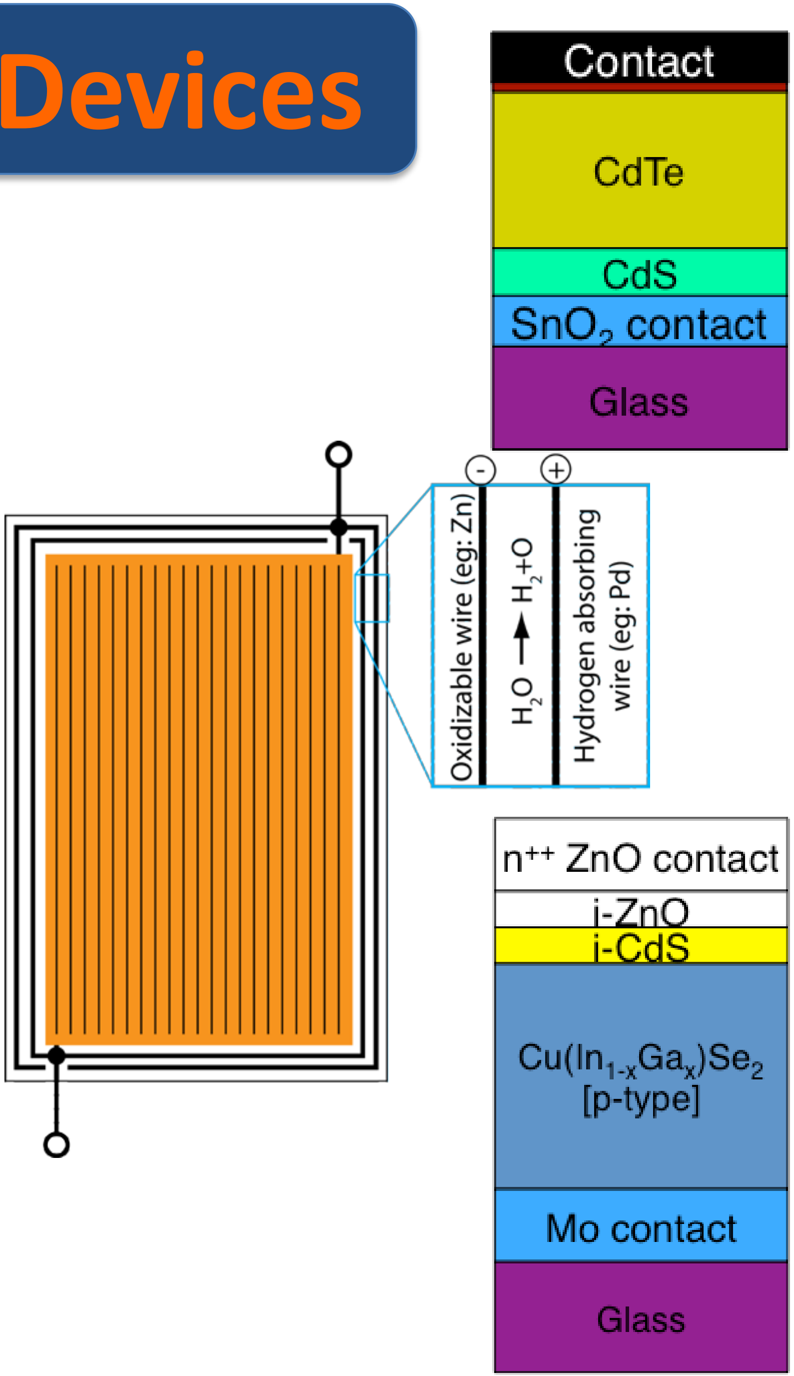
Sacrificial reactants

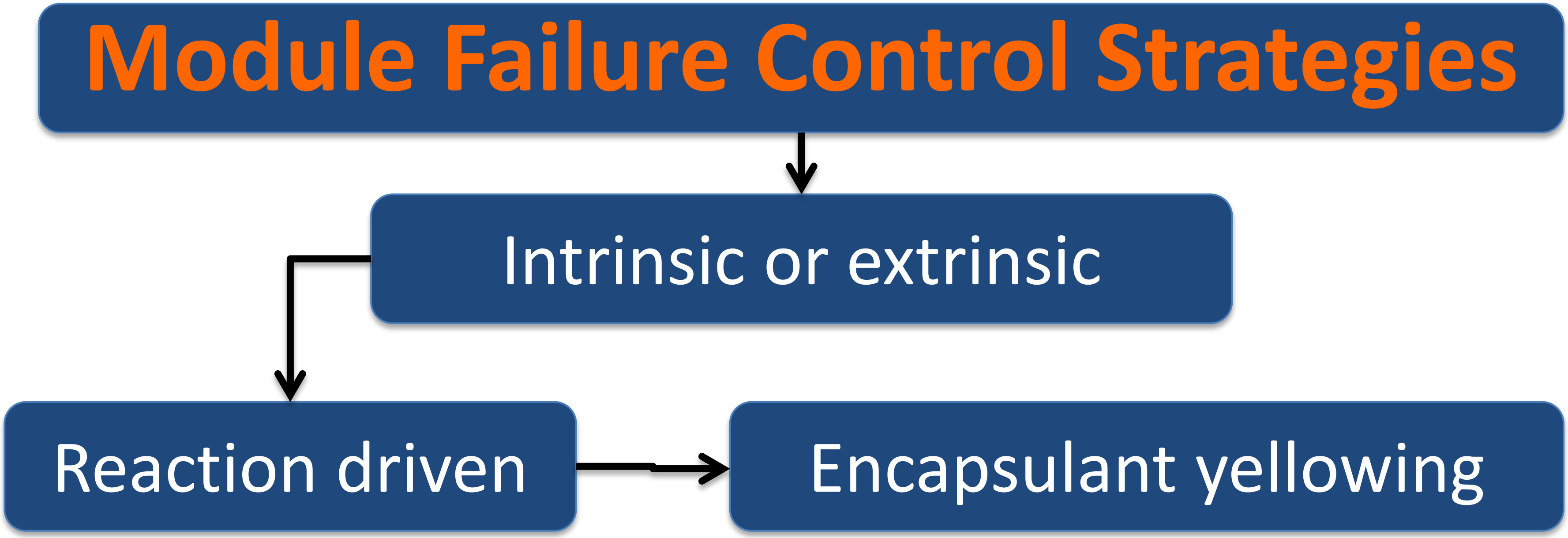
Electrochemical protection

Diffusion barriers in microelectronics incorporate sacrifical reactants. Galvanized iron uses electrochemistry to protect the iron

Water in Thin Film Devices

- TCO degradation: reaction with water.
- Consider active electrochemical control.
- Electrolyze the water in the module. Scavange the oxygen and hydrogen.
- Sacrificial wires integrated into module boundaries coupled to the output electrodes to drive electrolysis.





Module Failure Control Strategies

Intrinsic or extrinsic

Reaction driven

Encapsulant yellowing

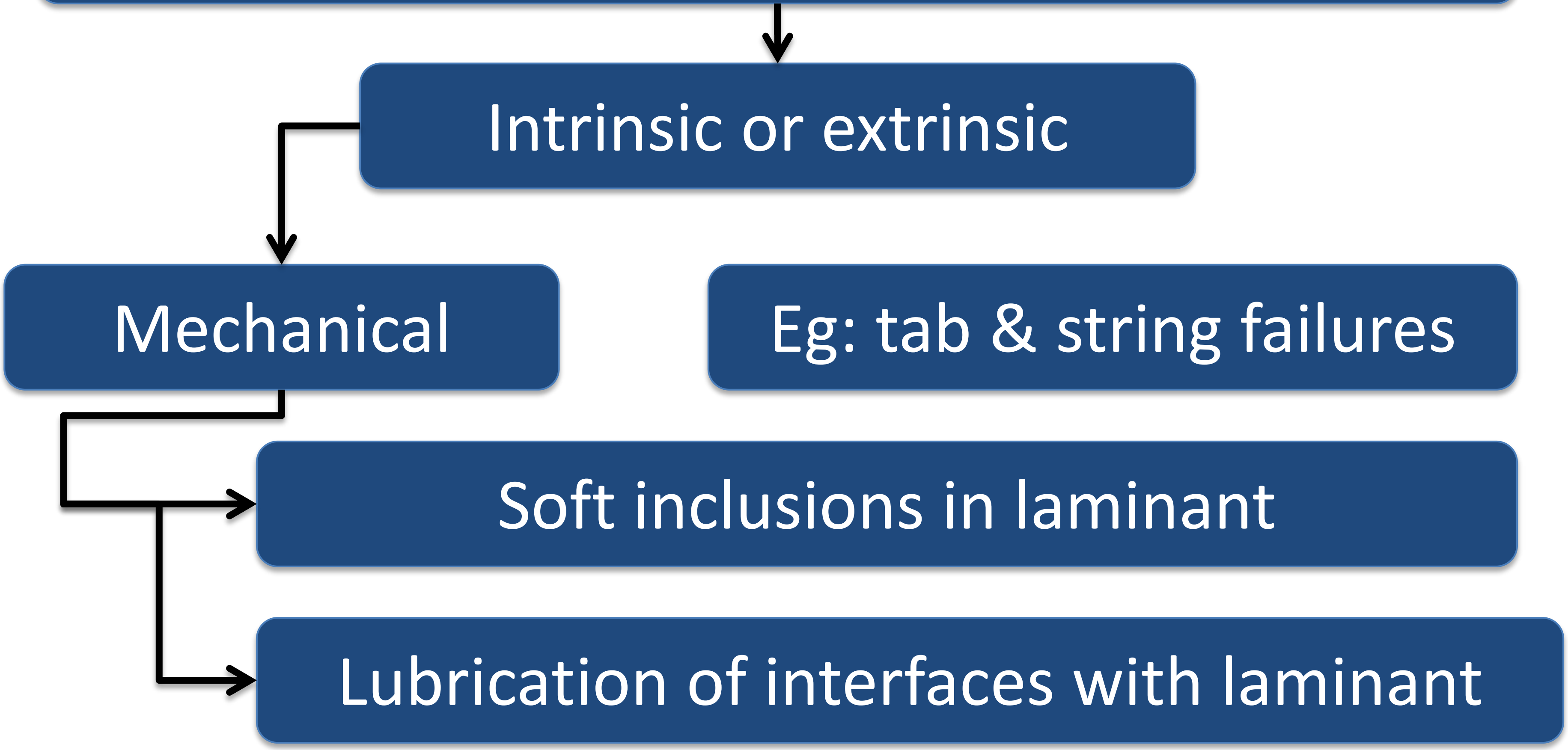
Any organic (or amorphous network) that absorbs a photon breaks a bond. That bond may not reform if it has alternatives.

Selective absorbers

Molecular scavangers

Stable molecules

Module Failure Control Strategies



Intrinsic or extrinsic

Mechanical

Eg: tab & string failures

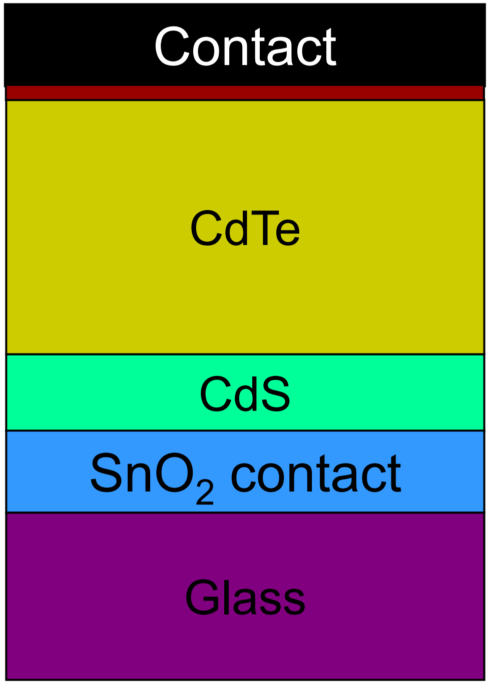
Soft inclusions in laminant

Lubrication of interfaces with laminant

The interface between the device/interconnect and the laminant can be adjusted. This can reduce mechanically-driven failures.

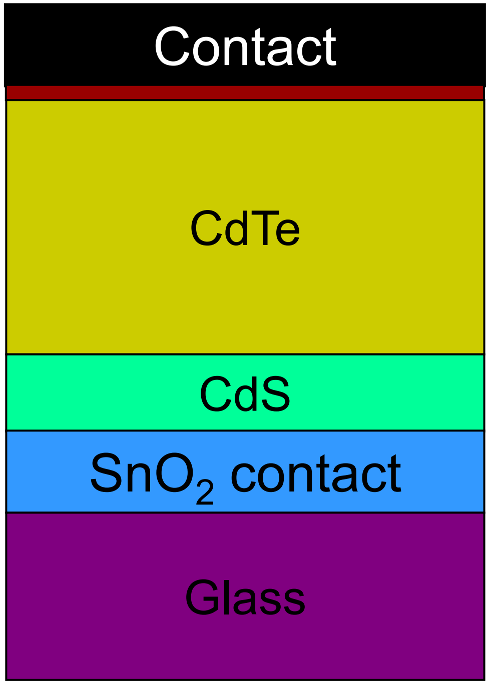
CdTe Thin Film Devices

- Thermodynamically unstable:
- SnO_2/CdS
- CdS/CdTe
- CdTe/[Cu_2Te]/C:Cu



CdTe Thin Film Devices

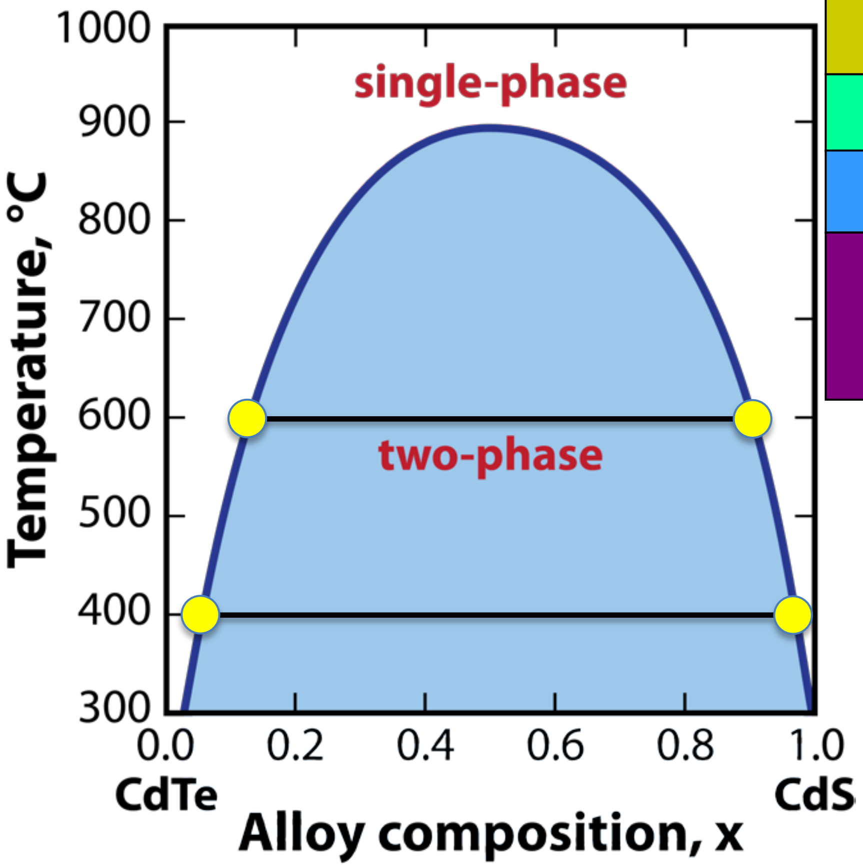
- CdS/CdTe interface: intrinsically stable if in equilibrium (but it is not). However, kinetics probably makes it adequately metatstable.



Heat-up: mutual dissolution

Cool-down: precipitation of alloy resulting in regrowth of a graded junction

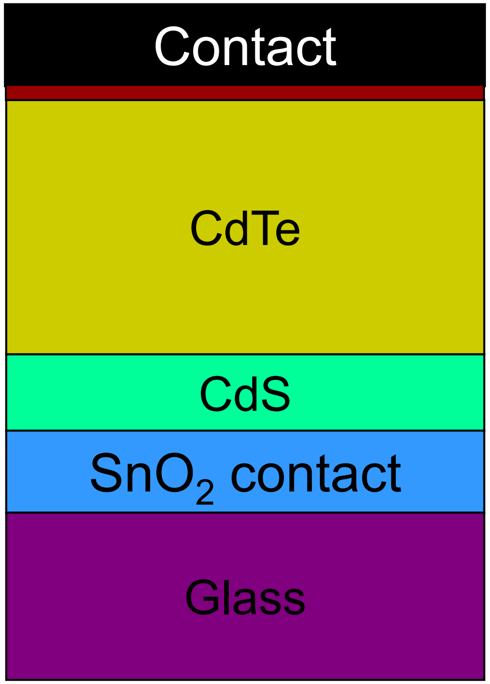
When transport freezes out local second phase preciptiation is possible.



At some temperature transport freezes out. That determines the composition grading at the heterojunction.

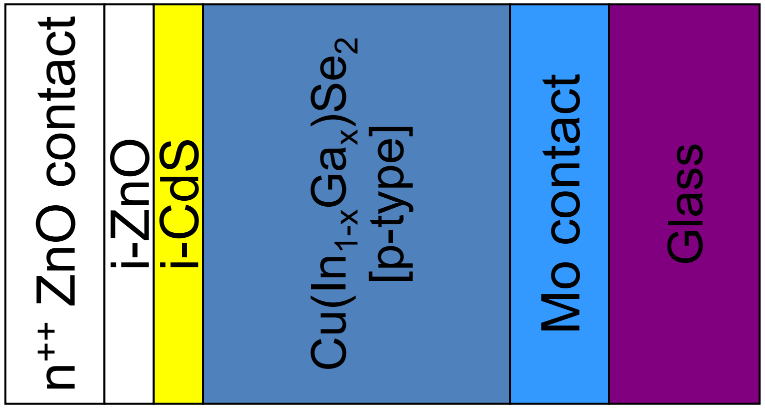
CdTe Thin Film Devices

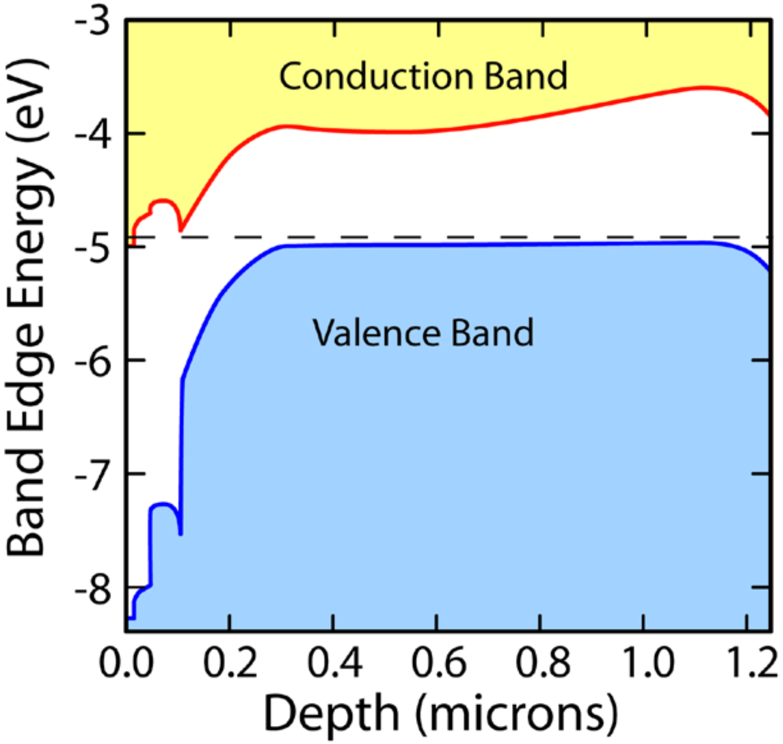
- SnO_2/CdS interface: Interdiffusion can be expected (thermodynamically favored, kinetically limited).
- Interdiffusion in this case yields Cd_2SnO_4 (cadmium stannate), an excellent TCO, comparable to or better than SnO_2.
- As long as the CdS is not consumed you should not be sensitive to interdiffusion.
- Diffusion kinetics is by far the fastest during CdTe deposition so further degradation is unlikely during operation.



CIGS Thin Film Devices

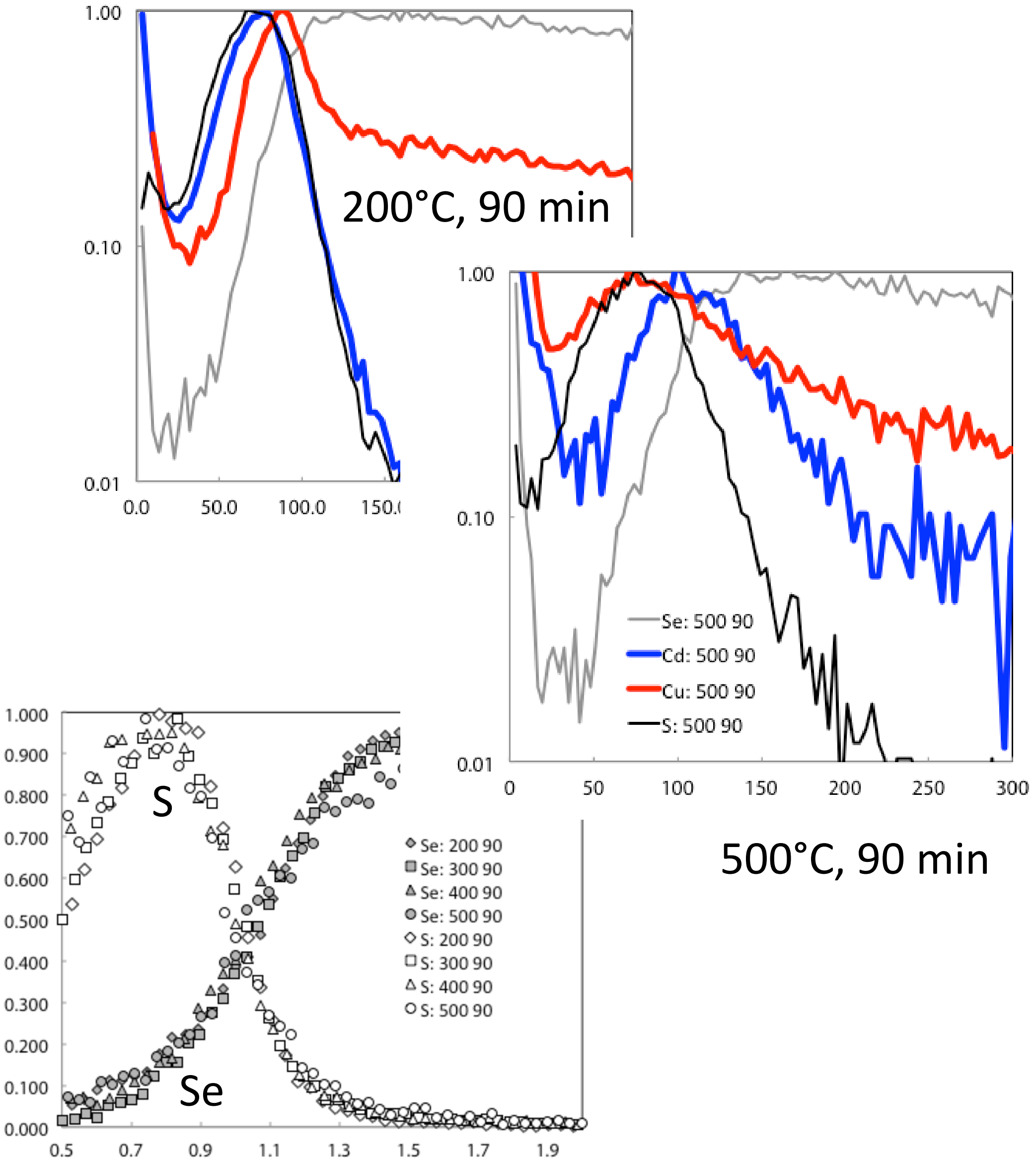
- Thermodynamically unstable:
- TCO: see I. Repins talk.
- ZnO/CdS
- CdS/CIGS
- CIGS point defects
- CIS/CGS (gradient)
- CIS/[$MoSe_2$]/Mo





CIGS Thin Film Devices

- **CdS/CIGS Interface:**
- We measured CdS/CIS interdiffusion by SIMS on epilayers and polycrystals as a function of anneal temperature.
- Diffusion turns on around 400°C.
- Some evidence of a Cd(CuIn)(S,Se)$_2$ compound.
- No group VI movement.
- Diffuses rapidly in grain boundaries.
- Probably not much going on under operating conditions.



CIGS Thin Film Devices

- **Mo/$MoSe_2$/CIGS:**
- Reaction with water similar to Al/Se reaction with water (but slower).
- Se loss would reduce p-type doping at the back contact, increasing resistance.
- $MoSe_2$ loss could result in a Schottky rather than an ohmic contact.

$$MoSe_2 + 2H_2O \rightarrow MoO_2 + 2H_2Se$$

Endothermic but if H_2Se is lost as a gas the law of mass action will drive it to products.

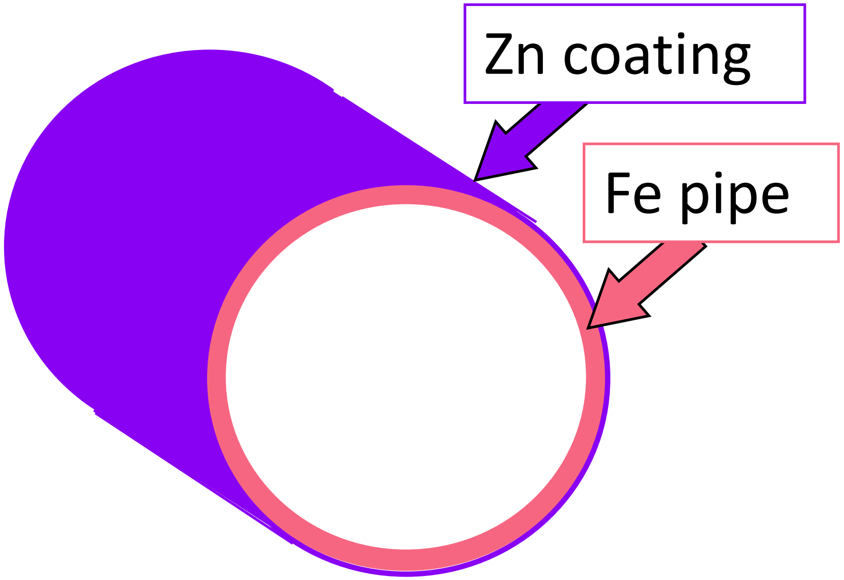
ΔH_f $MoSe_2$: -234 kJ/mol
ΔH decomposition $MoSe_2$ to Mo + $Se_2(g)$: 378 kJ/mol
ΔH_f MoO_2: -586 kJ/mol
ΔH_f H_2Se: -29 kJ/mol
ΔH_f H_2O: -242 kJ/mol

Conclusions

- Module failures can be divided into diffusion-based, reaction/chemistry based, and mechanical failures.
- Barriers and sacrificial materials may help but choice of materials for slow kinetics may be the only real solution.
- Metastable phenomena may occur driven by changes in the Fermi level in the solid. However, kinetics makes long-range transport unlikely.
- Transient effects probably due to change of charge state of deep defects or clusters.

Electrochemistry:
Application -- corrosion protection

Electrolytic protection controls where corrosion occurs
Example: Zn protection of Fe



Because the Zn is higher on the electrochemical series than Fe, it corrodes in preference to the Fe.

Most of the available oxidizing species react with the Zn.

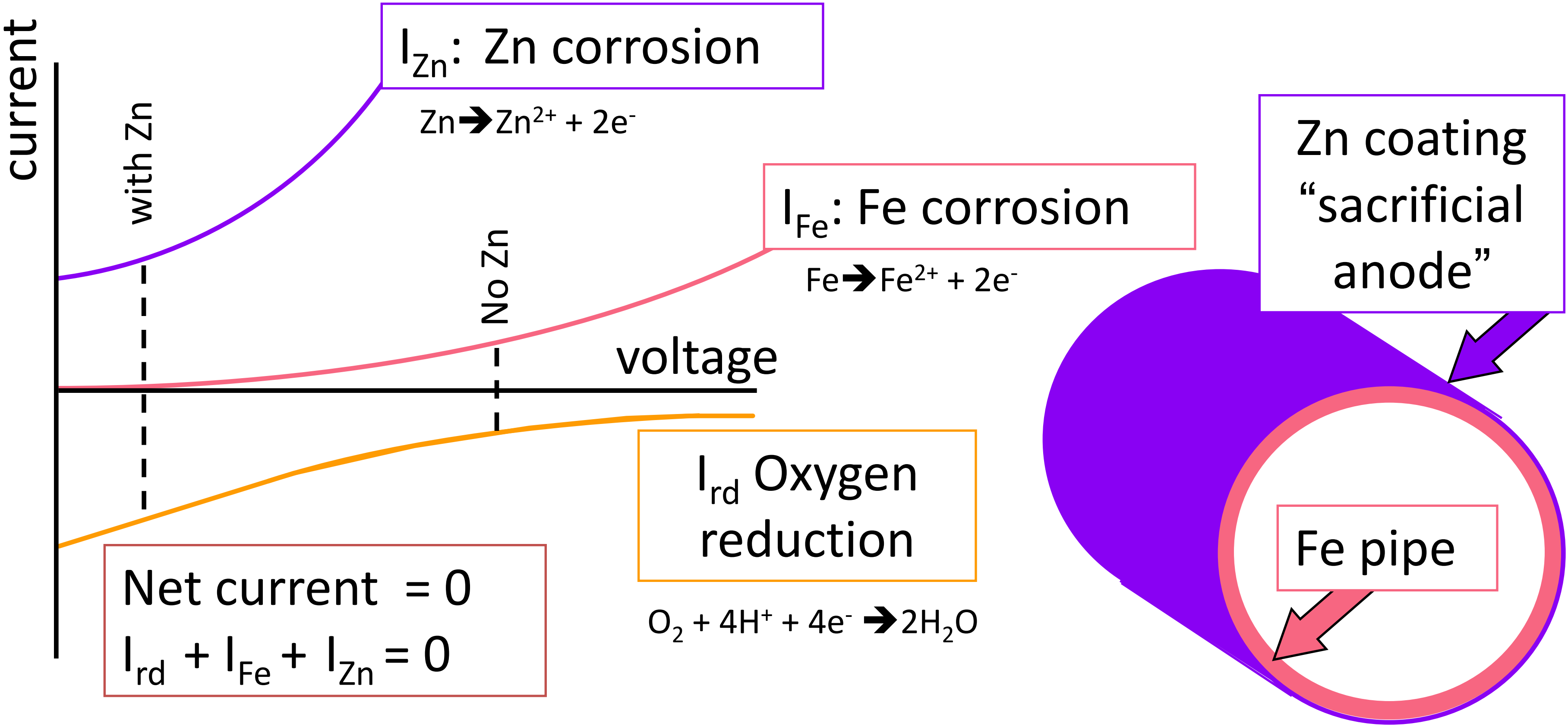
Until the Zn is completely gone it protects the Fe.

<u>The electrochemical series:</u>

$Mg \rightarrow Mg^{+2} + 2e^-$	+2.37	V
$Al \rightarrow Al^{+3} + 3e^-$	+1.66	V
$Zn \rightarrow Zn^{2+} + 2e^-$	+0.76	V
$Fe \rightarrow Fe^{2+} + 2e^-$	+0.44	V
$H_2 \rightarrow H^+ + e^-$	0.00	V
$Cu \rightarrow Cu^{2+} + 2e^-$	-0.34	V

Electrochemistry:
Application -- corrosion protection

The protection reaction can be quantized by looking at the current/voltage curve (voltammogram) for the reactions:



I_{Zn}: Zn corrosion

$Zn \rightarrow Zn^{2+} + 2e^-$

I_{Fe}: Fe corrosion

$Fe \rightarrow Fe^{2+} + 2e^-$

I_{rd} Oxygen reduction

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

Net current = 0

$I_{rd} + I_{Fe} + I_{Zn} = 0$

Zn coating “sacrificial anode”

Fe pipe