Ultrafast Dynamics of Excited Electrons in Materials for Energy Application

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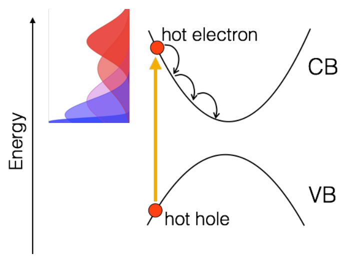
Ultrafast Dynamics of Excited Carriers



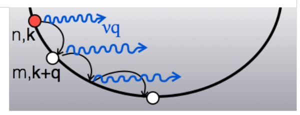
Understand excited ("hot") carriers in materials:

- Energy distribution vs. time
- Timescale (10–100 fs) for energy loss
- Transport and mean free paths

Codes: Quantum ESPRESSO, BerkeleyGW, EPW. We used in-house modified versions

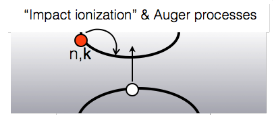
Two ultrafast (<1ps) mechanisms for hot carriers to lose energy

Electron – phonon scattering

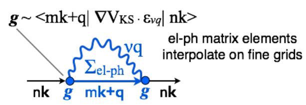


Electron – electron scattering

"Impact ionization" & Auger processes

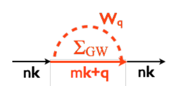


Use perturbation theory



$(\tau_{nk}^{-1})_{el\text{-}ph} \sim \mathrm{Im}(\Sigma_{nk})_{el\text{-}ph} = \mathrm{Im}\, g^2 GD$

DFT + Wannier electron-phonon approach



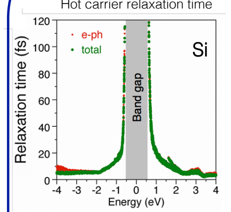
$(\tau_{nk}^{-1}) \sim \mathrm{Im}(\Sigma_{nk})_{el\text{-}el} = \mathrm{Im}\, G\cdot(\varepsilon_{RPA}^{-1} V)$

Ab initio GW method

Relaxation time of carrier in state n,k: $(\tau_{nk})^{-1} = \mathrm{Im}(\Sigma_{nk})_{el\text{-}ph} + \mathrm{Im}(\Sigma_{nk})_{el\text{-}el}$

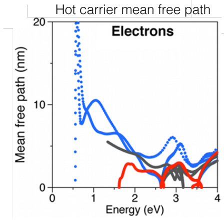
Hot Carriers in Silicon Solar Cells

Hot carrier relaxation time



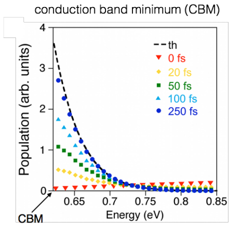
Fast (10 fs) away from band edge
Slower (100 fs) near the band edge

Hot carrier mean free path



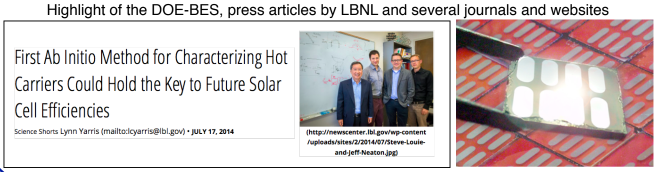
Mean free paths ~5–10 nm in Si
Anisotropy: [100] most favorable

Hot electron thermalization near the conduction band minimum (CBM)



Excellent agreement with experiment: thermalization in 250–300 fs near CBM

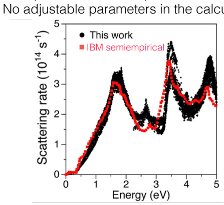
Highlight of the DOE-BES, press articles by LBNL and several journals and websites



Reference: M. Bernardi, D. Vigil-Fowler, J. Lischner, J.B. Neaton, S.G. Louie, Phys. Rev. Lett. 112, 257402 (2014)

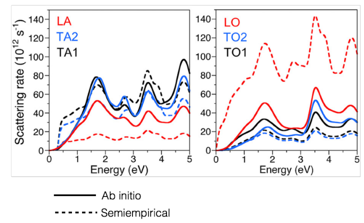
Hot Electrons in GaAs

Compute ~50 trillion el-ph matrix elements
No adjustable parameters in the calculation

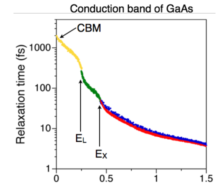


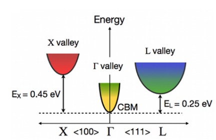
Semiempirical: Multiple parameters for el-ph coupling

Where did the "old" (semiempirical) calculations go wrong?



Conduction band of GaAs





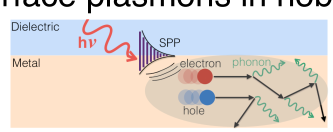
Experiment: pump with 2 eV light yields three time decay signals: ~40 fs, ~200 fs, 1.5 ps

Excellent agreement with pump-probe experiments

Help resolve a long-standing controversy on HCs in GaAs

Reference: M. Bernardi, D. Vigil-Fowler, C.S. Ong, J.B. Neaton, S.G. Louie, PNAS 112, 5291 (2015)

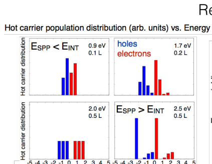
Generation and relaxation of hot carriers from surface plasmons in noble metals

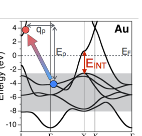


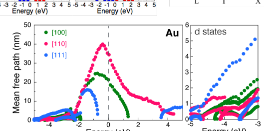
Energy and momentum conserving transitions induced by surface plasmon polaritons (SPPs) generate hot carriers with a distribution of energies (in a probabilistic sense)

Results for Au, Ag and Cu show similar trends

Hot carrier population distribution (arb. units) vs. Energy



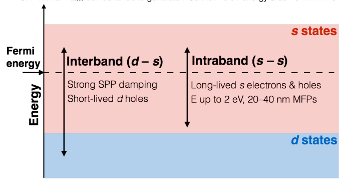




Application to photocatalysis with hot carriers

Two regimes for SPP-to-hot carrier conversion: intraband vs. interband

SPP with E < E_INT can be tuned to generate HCs with ~2 eV energy & 20-40 nm MFPs

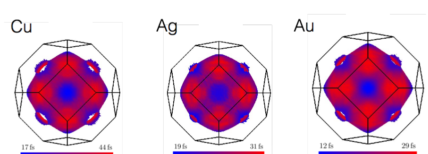


Silver may be better than gold for hot carriers from SPPs

Reference: M. Bernardi, J. Mustafa, J.B. Neaton, S.G. Louie, Nature Commun. 6, 7044 (2015)

Carrier Transport from First Principles

Electron-phonon (el-ph) scattering controls the resistivity of metals at room temperature
Using importance sampling, we map the el-ph relaxation times (RT) on the Fermi surface



Relaxation times on the Fermi surface

Conductivity $\sigma_{i,j} = e^2 \sum_{n,\mathbf{k}} \tau_{n,\mathbf{k}} v_{n,\mathbf{k},i} v_{n,\mathbf{k},j} \left(-\partial f/\partial E\right)$

Typical ab initio calculations combine DFT bands with the RT as a parameter
Using GW and ab initio el-ph RTs, we can predict the resistivity of noble metals within 10% of exp.

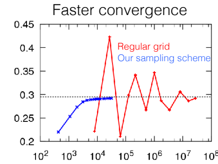
Accuracy

Resistivity (μOhm cm)

	Calculated	Experimental	
	GW+ab initio RT	SC	PC
Cu	1.57	1.52	1.74
Ag	1.99	1.49	1.68
Au	1.95		2.26

SC = single crystal PC = polycrystalline

Faster convergence



Reference: J. Mustafa, M. Bernardi, J.B. Neaton, S.G. Louie, Submitted.

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