Ben-Gurion University
of the Negev

Enhancing the optical properties of semiconductor nanostructures with metal films and surface plasmons

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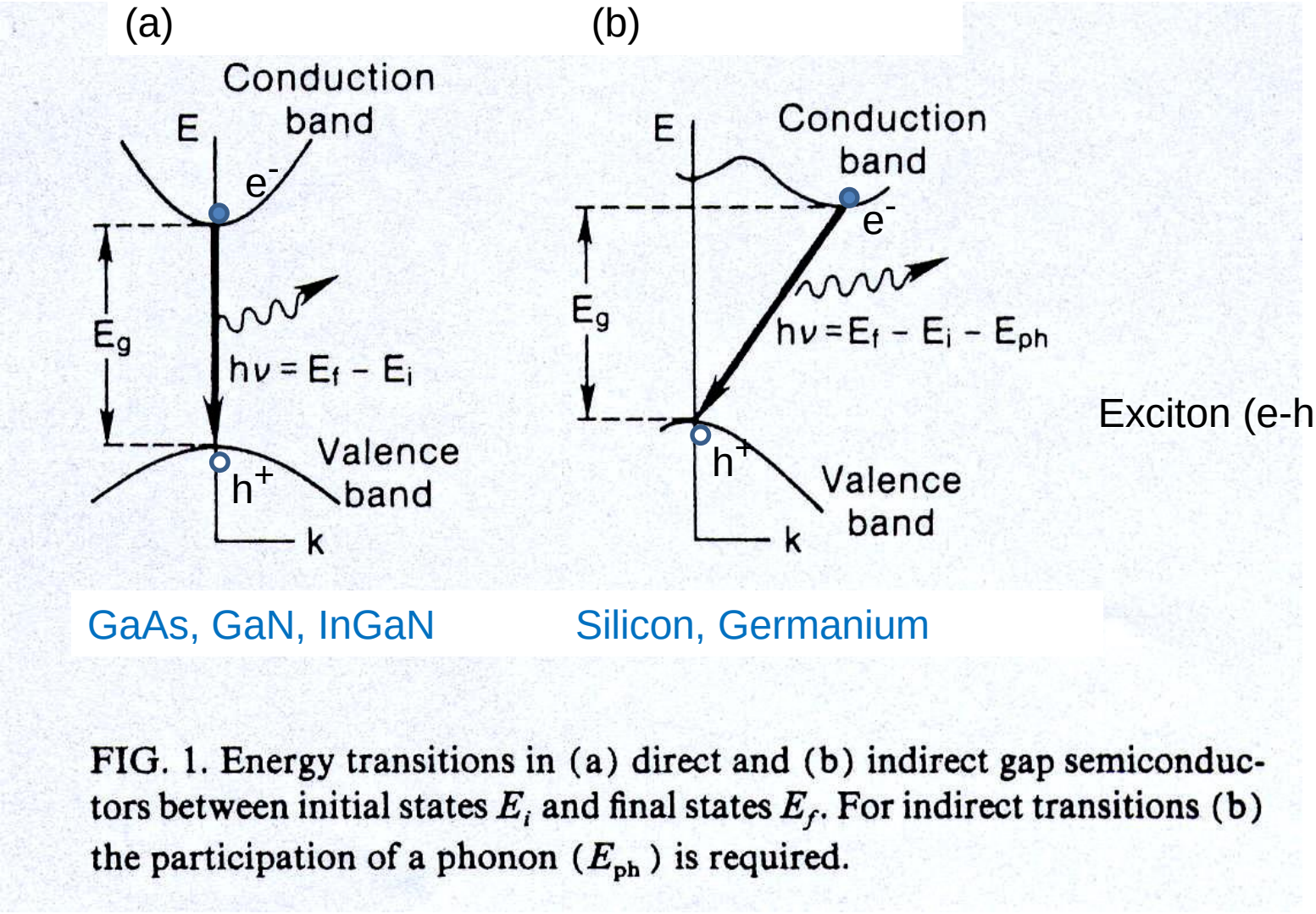
An important focus in nanostructures is the design of plasmonic metal/semiconductor composite structures to obtain novel optical device properties for applications in biological labeling/sensing, light-emitting diodes, lasers, and solar cells.

Outline of Talk

1. Growth of **GaAs/AlAs/GaAs core-shell nanowires (NWs)**, **InGaN/GaN QWs**, and **Si nano-crystals (SiNCs)** (i.e., quantum dots (QDs))
2. Deposition of thin metal films: Gold, Silver and Aluminum films on the three material systems with dimensionalities of (*i*) QWs, (*ii*) NWs, and (*iii*) QDs
3. Spatially, Spectrally, and temporally-resolved cathodoluminescence (CL): *e*-beam probe and easy penetration of thin metal films
4. Assess coupling of **excitons** (*e*-*h* pairs) to **surface plasmon polaritons (SPPs)**
5. Measure changes in the spontaneous emission rate (**SER**) of excitons in the nanowires and quantify the Purcell Enhancement Factor (F_p)



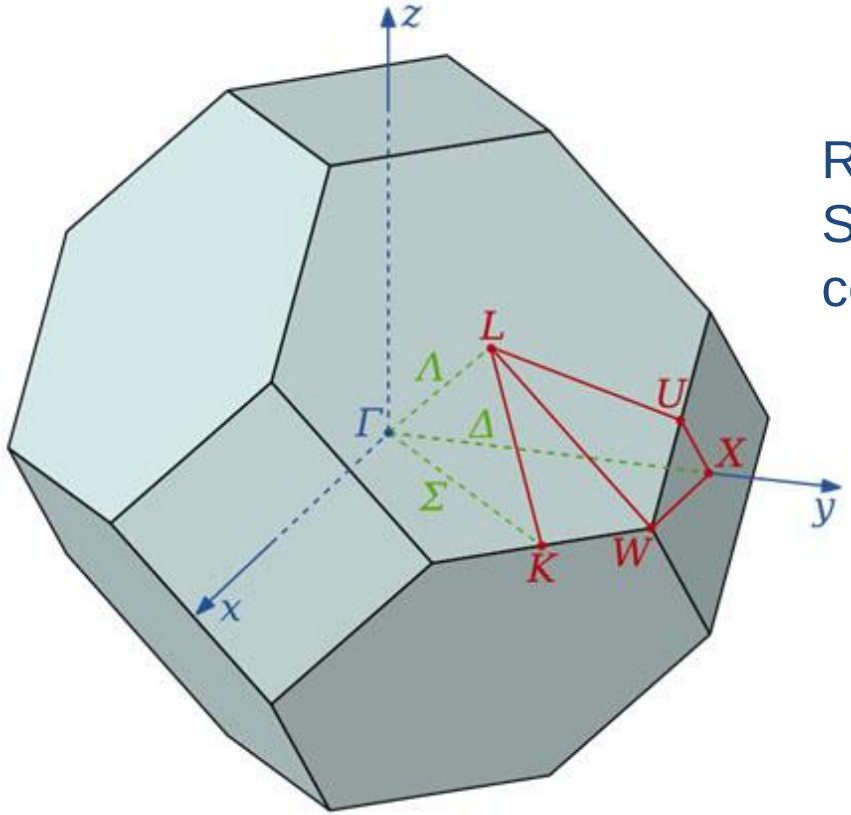
Exciton (e-h pair)

GaAs, GaN, InGaN

Silicon, Germanium

FIG. 1. Energy transitions in (a) direct and (b) indirect gap semiconductors between initial states E_i and final states E_f. For indirect transitions (b) the participation of a phonon (E_{ph}) is required.

The face centered cubic (fcc) Brillouin Zone



Relevant Semiconductors:
Si, Ge, GaAs and many III-V compounds

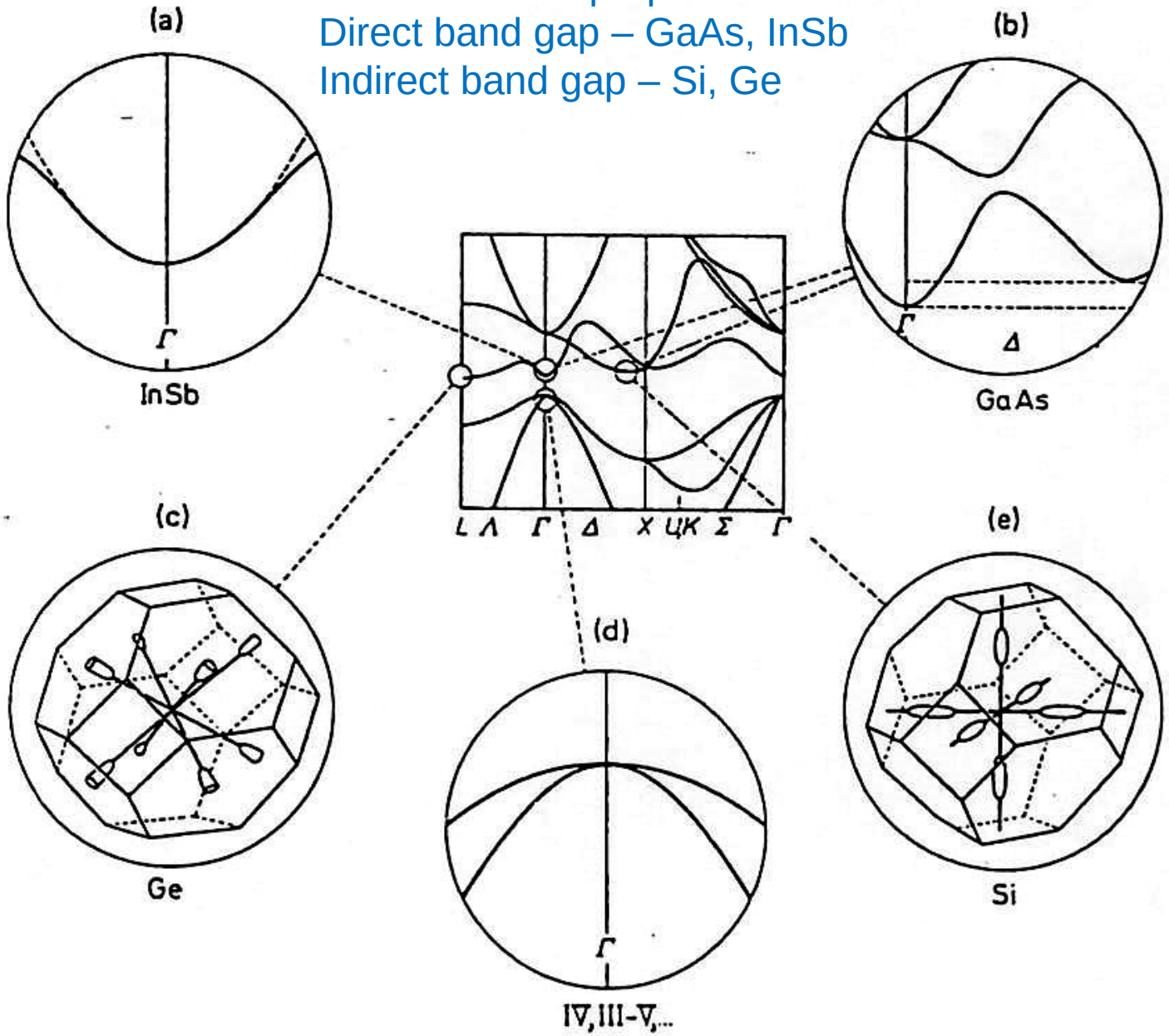
Special symmetry points:

X=(0,1,0)2π/a, L=(1/2,1/2,1/2) 2π/a,

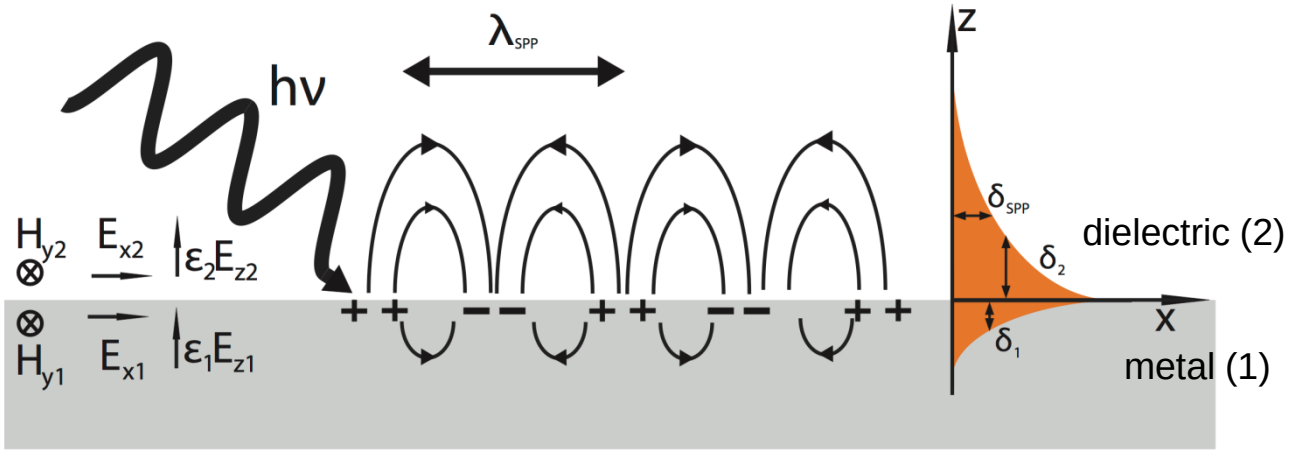
K=(3/4,3/4,0)2π/a, W=(1/2,1,0) 2π/a,

U=(1/4,1,1/4)2π/a

Band structure properties
Direct band gap – GaAs, InSb
Indirect band gap – Si, Ge



Basics of Surface Plasmon Polaritons (SPPs)

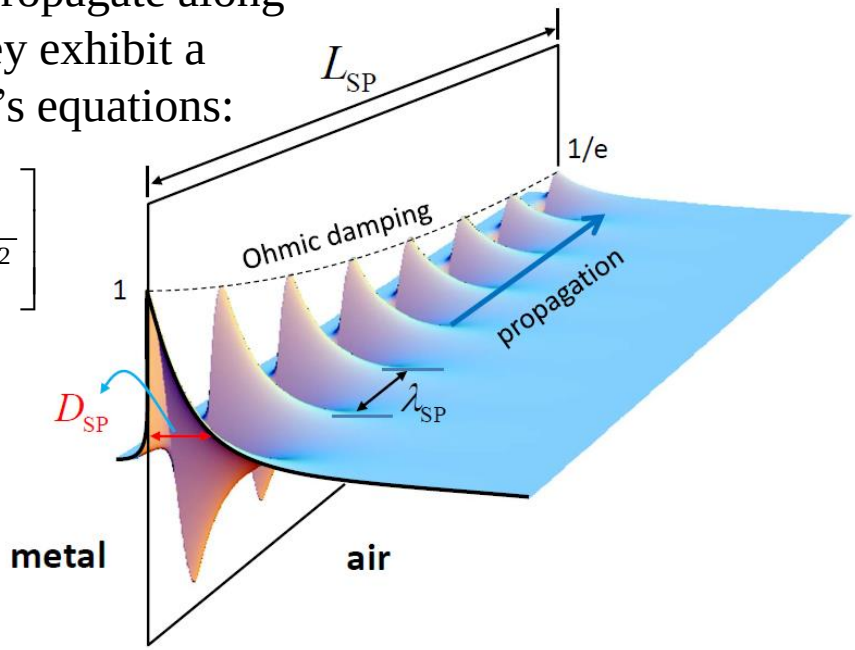


SPPs are oscillations in the charge density that propagate along the interface between a metal and dielectric. They exhibit a complex wavevector from solutions to Maxwell's equations:

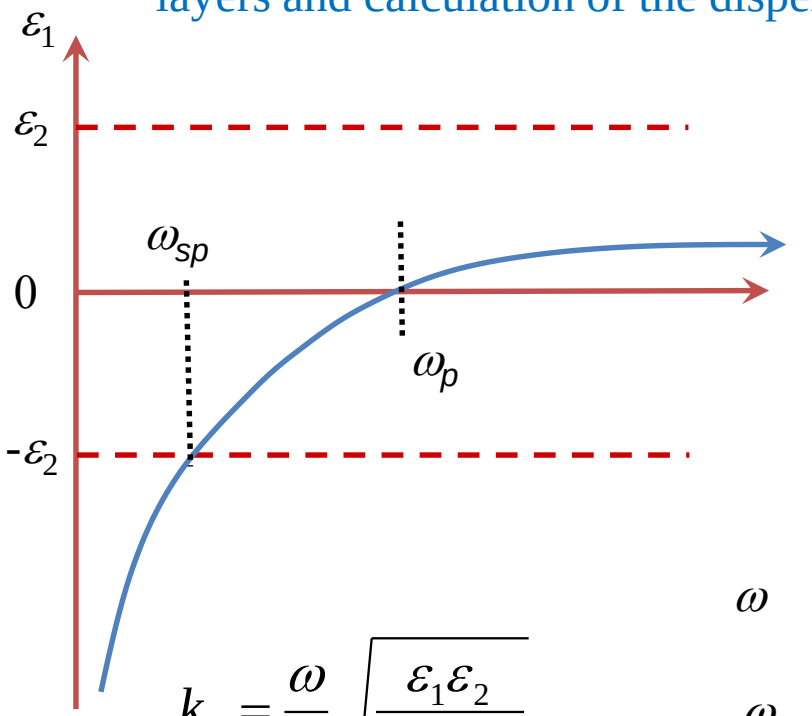
$$k_x = k_x' + ik_x'' = \left[\frac{\omega}{c}\left(\frac{\varepsilon_1'\varepsilon_2}{\varepsilon_1'+\varepsilon_2}\right)^{1/2}\right] + i\left[\frac{\omega}{c}\left(\frac{\varepsilon_1'\varepsilon_2}{\varepsilon_1'+\varepsilon_2}\right)^{3/2}\frac{\varepsilon_1''}{2(\varepsilon_1')^2}\right]$$

$$L_{SP} = \frac{1}{2k_x''} \qquad \text{(Propagation length)}$$

$$z_i = \frac{\lambda}{2\pi}\left(\frac{|\varepsilon_1'|+\varepsilon_2}{\varepsilon_i^2}\right)^{1/2} \qquad \text{(E-field decay length)}$$



Examination of the dielectric constants for both the metal (ε_1) and dielectric (ε_2) layers and calculation of the dispersion relation $\omega(k_x)$ for surface plasmons.

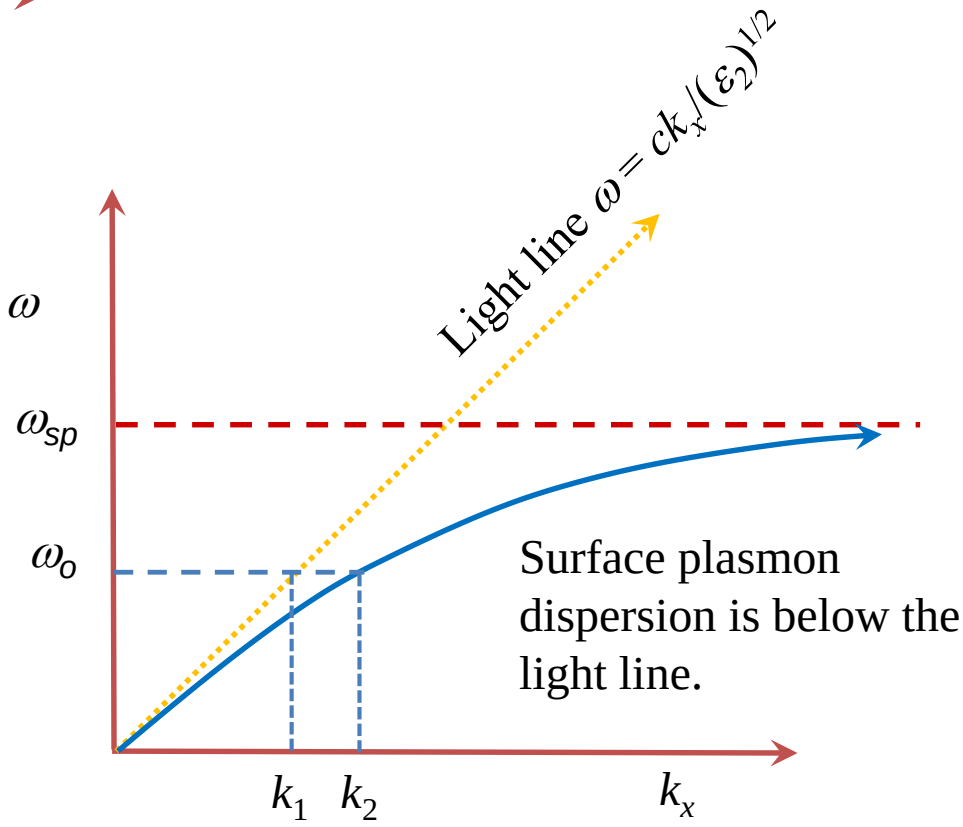


$$n^2 = \varepsilon_1(\omega) = 1 - \frac{\omega_p^2}{\omega^2}$$

$$k_x = \frac{\omega}{c}\sqrt{\frac{\varepsilon_1\varepsilon_2}{\varepsilon_1 + \varepsilon_2}}$$

1) For small ω, $\varepsilon_1 \rightarrow -\infty$ and $k_x \approx (\omega/c)(\varepsilon_2)^{1/2} = \omega/v_d$

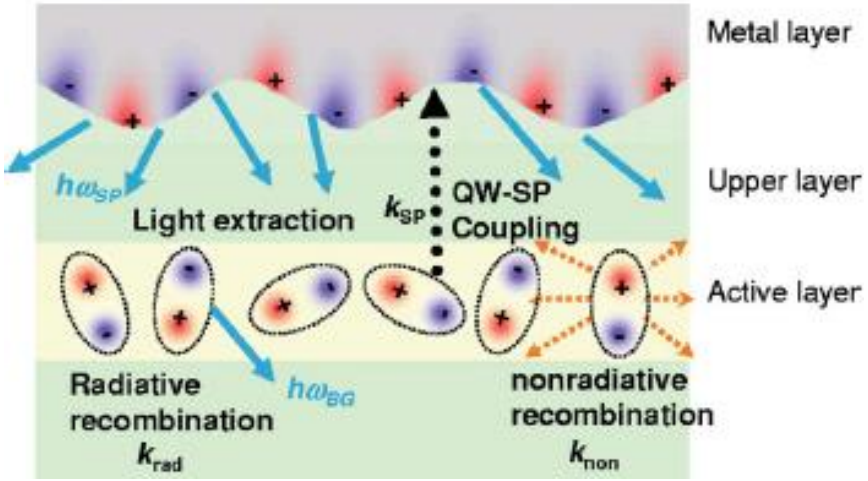
2) At $\omega = \omega_{sp}$, $\varepsilon_1 \rightarrow -\varepsilon_2$ (from below) and $k_x \rightarrow +\infty$



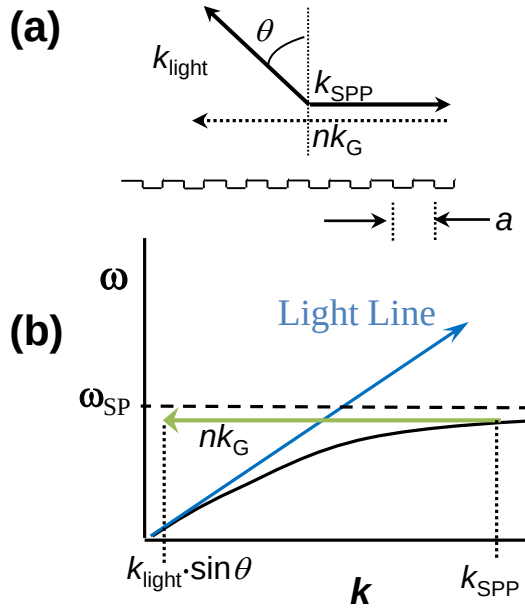
Surface plasmon dispersion is below the light line.

In general, the phase velocity of SPPs ($v_{ph} = \omega/k$) is less than that of light in the dielectric adjacent to a metal film.

1) Exciton (***e-h*** pair) to SPP coupling (quantum well, wire or dot)
2) SPP conversion to a photon



Model of the exciton-SPP coupling mechanism. (K. Okamoto at al. APL **87**, 071102 (2005))



Plasmon DOS:

$$\rho_{2D}(\omega) = \frac{k}{2\pi}\frac{1}{v_g}$$

$$v_g = \frac{\partial\omega}{\partial k} \to 0$$

SPP dispersion relation

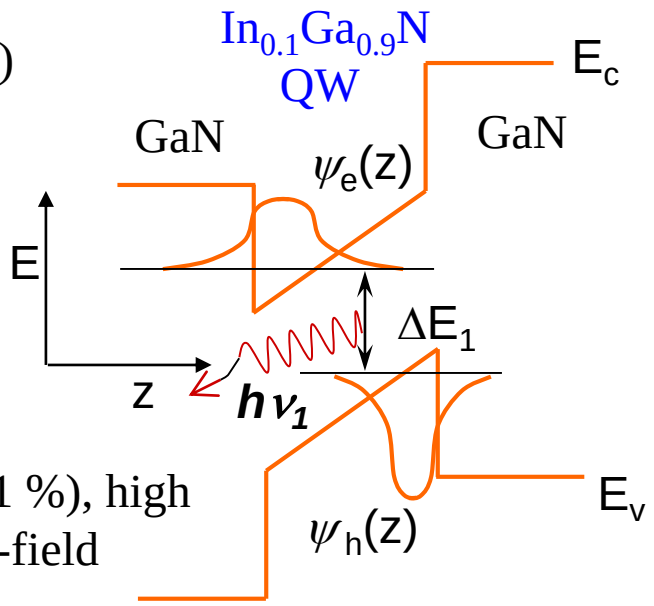
The decoupling of SPPs into light is described by the kinematic equation: $\mathrm{Re}[k_{SP}(\omega)] - nk_G = (\omega/c)\sin(\theta)$.

- Scattering occurs by the surface/interface roughness or grain boundaries of the polycrystalline metal film.
- Momentum change associated with the scattering enables a matching with the ω vs *k* light dispersion relation.
- Roughness is a superposition of many gratings with different $\boldsymbol{k}_G$.

Challenges and Motivation for increasing the SER in quantum heterostructures / nanostructures

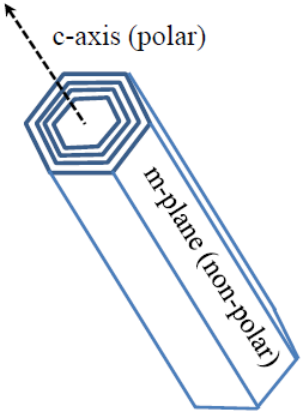
1. $In_xGa_{1-x}N$/GaN QWs used for LEDs / Lasers

- Growth on *c*-plane (0001) Sapphire : Conventional MOCVD techniques lead to a high threading dislocation density (~10^8 – 10^9 cm^{-2}) and V-pit defects, owing to the large lattice mismatch between wurtzite (hexagonal) GaN and Sapphire.
- Large piezo-electric fields (~10^6 V/cm) lead to a reduced oscillator strength.
- Thus, the non-radiative recombination rate ($R_{NR} = 1/\tau_{NR}$) will compete with the radiatiatve rate ($R_R = 1/\tau_R$).
- For metal-coated QWs, coupling between excitons and SPPs may lead to a larger R_R for improved IQE for opto-electronics and overcoming "green gap" in LED performance.



Large strain (~1 %), high piezoelectric **E**-field

Challenges and Motivation for increasing the SER in quantum heterostructures / nanostructures

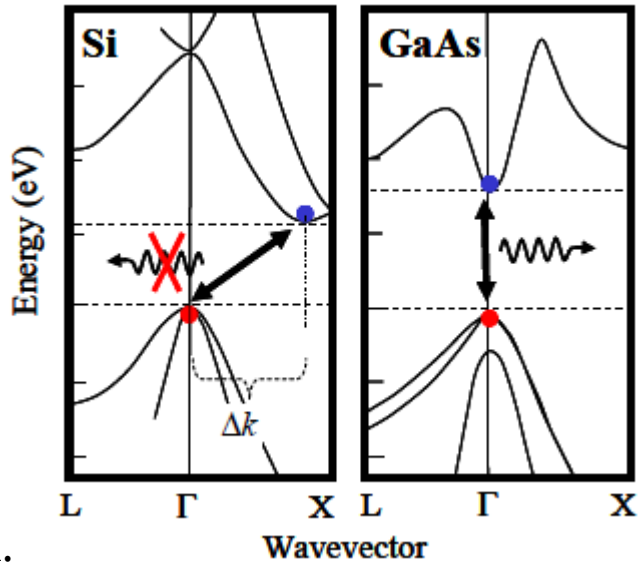


2. III-V core-shell nanowires possess a large surface recombination velocity (*S*).

- For bare GaAs wires, $\tau_{NR} = d/2S \approx 10^{-12}$ s for a NW diameter (d) of 30 nm and $S = 10^6$ cm/s.
- For GaN wires, S ~ 10^4 cm/s, but the piezoelectric fields can limit the IQE, as seen for the QWs.

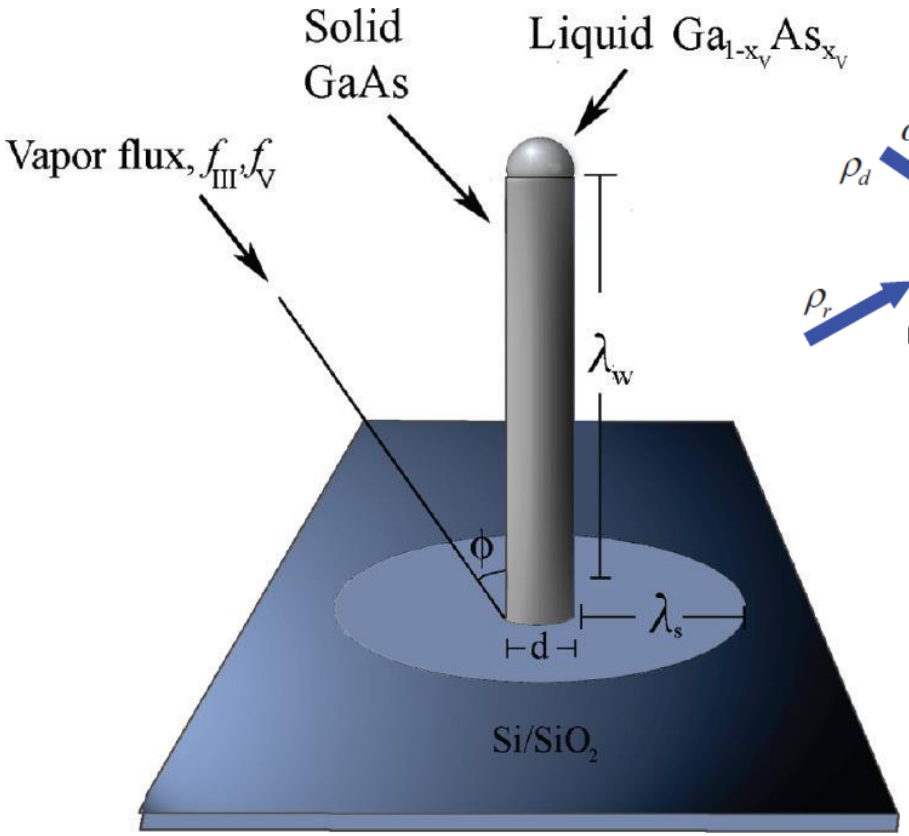
3. Si Nanocrystals (SiNCs)

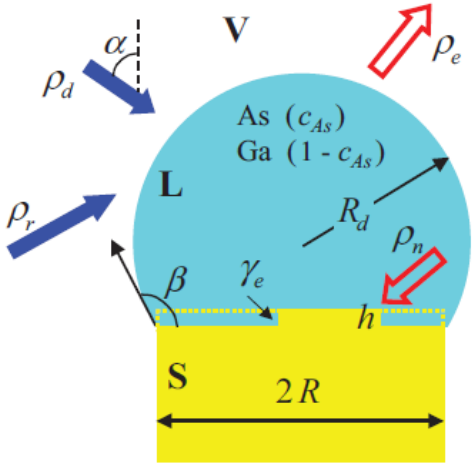
- Bulk Si is an indirect bandgap material which leads to long *e-h* lifetimes (~ ms) due to the need for momentum conservation (phonons); limits usefulness in light emitters.
- However, for small SiNCs (D ~ 3 nm), Momentum conservation is partially relaxed due to Heisenberg uncertainty principle: Δk ~ 1/D.
- Quantum confinement leads to *quasi-direct* transition.
- Coupling of excitons to SPPs for metal-coated nanostructures for larger QE.



MBE Growth of GaAs nanowires: Vapor-Liquid-Solid (VLS) self-assisted catalyst-free growth

Gallium droplets are formed on the surface of the wafer which, on reaching a critical size, become supersaturated and begin nanowire growth.





The As fluxes feeding the (Ga, As) droplet:

ρ_d - direct beam

ρ_r - re-emitted by environment

ρ_e - evaporation

ρ_n - solid nucleation and growth by empty red arrows.

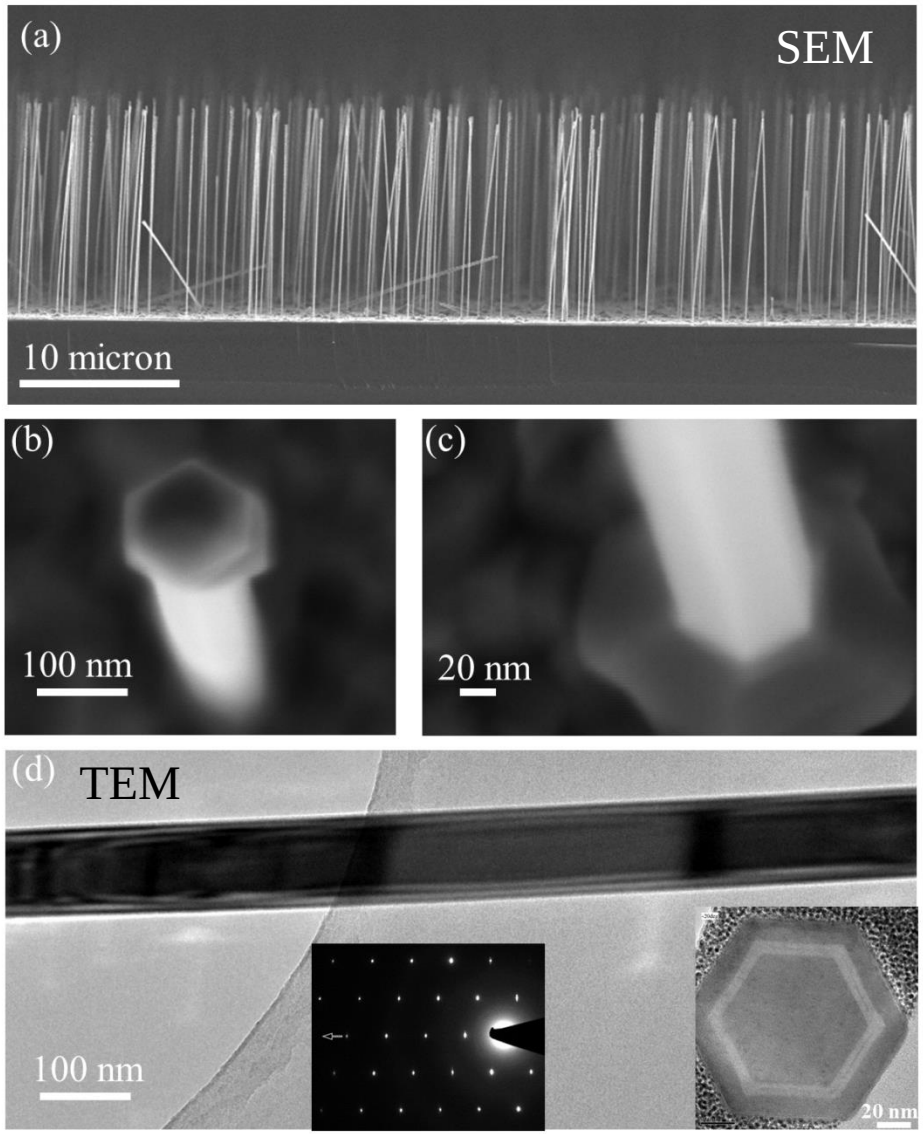
Only ρ_d is directional, due to As_4 beam incident at angle α.

"Predictive modeling of self-catalyzed III-V nanowire growth", F. Glas et. al., Phys. Rev. B **88**, 195304 (2013).

"Structural Phase Control in Self-Catalyzed Growth of GaAs Nanowires on Si(111)", P. Krogstrup, R. Popovitz-Biro, E. Johnson, M. Hannibal Madsen, J. Nygård and H. Shtrikman. Nano Letters **10**, 4475 (2010).

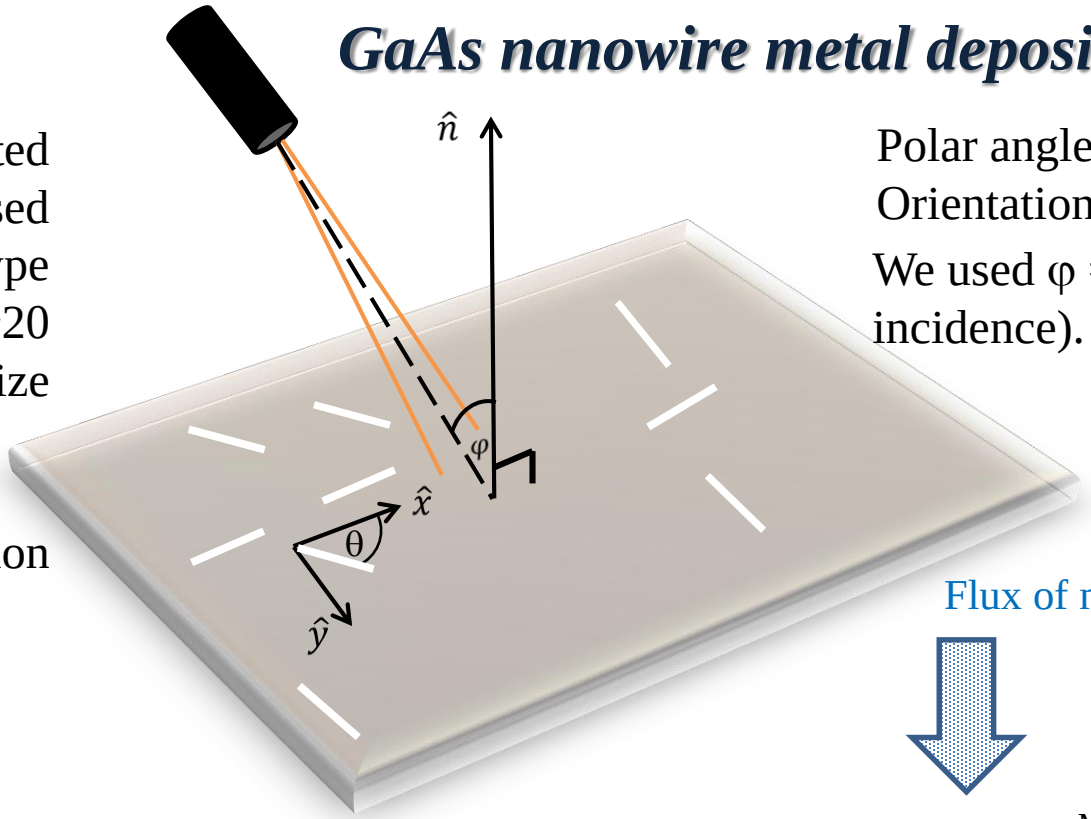
Nanowire growth:

- MBE growth of GaAs/AlAs/GaAs core-shell nanowires using the self-assisted VLS method
- Substrate: Si(111) with native oxide layer
- Water removal at ~200 ^{o}C, outgassing at ~600 ^{o}C
- Growth: initiated by condensation of Ga, $T_G \approx 640$ ^{o}C, and a V/III (As_4/Ga) ratio of ~100
- Uniform ~6 nm AlAs shell and ~12 nm GaAs capping layer, $T_G \approx 520$ °C
- Wire growth direction: ⟨111⟩, hexagonal shape with {011} facets
- Uniform diameter of ~100 nm, ~12 μm length, aspect ratio ~100, without tapering, and a pure zinc-blende structure (TEM).



GaAs nanowire metal deposition

- Nanowires were harvested and randomly dispersed onto heavily doped *p*-type Si wafers coated with ~20 nm-thick Al (to minimize charging in CL).
- Au and Al evaporation thickness (t_0) ~20 nm



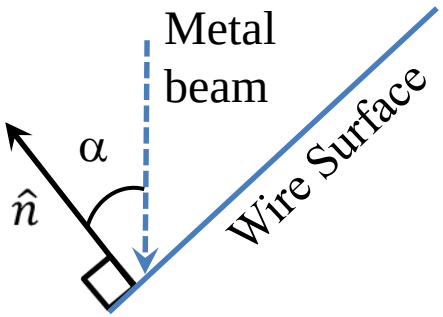
Polar angle (φ)
Orientation angle (θ)
We used φ = 0° (normal incidence).

1. Nanowire φ = 0 , any θ.

(Top view)

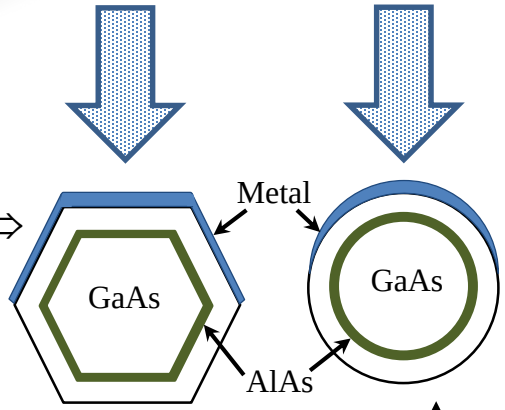
2. Nanowire φ > 0 , θ = 0.

Si(111) p^+-doped



$t = t_0 \cos\alpha \Rightarrow$

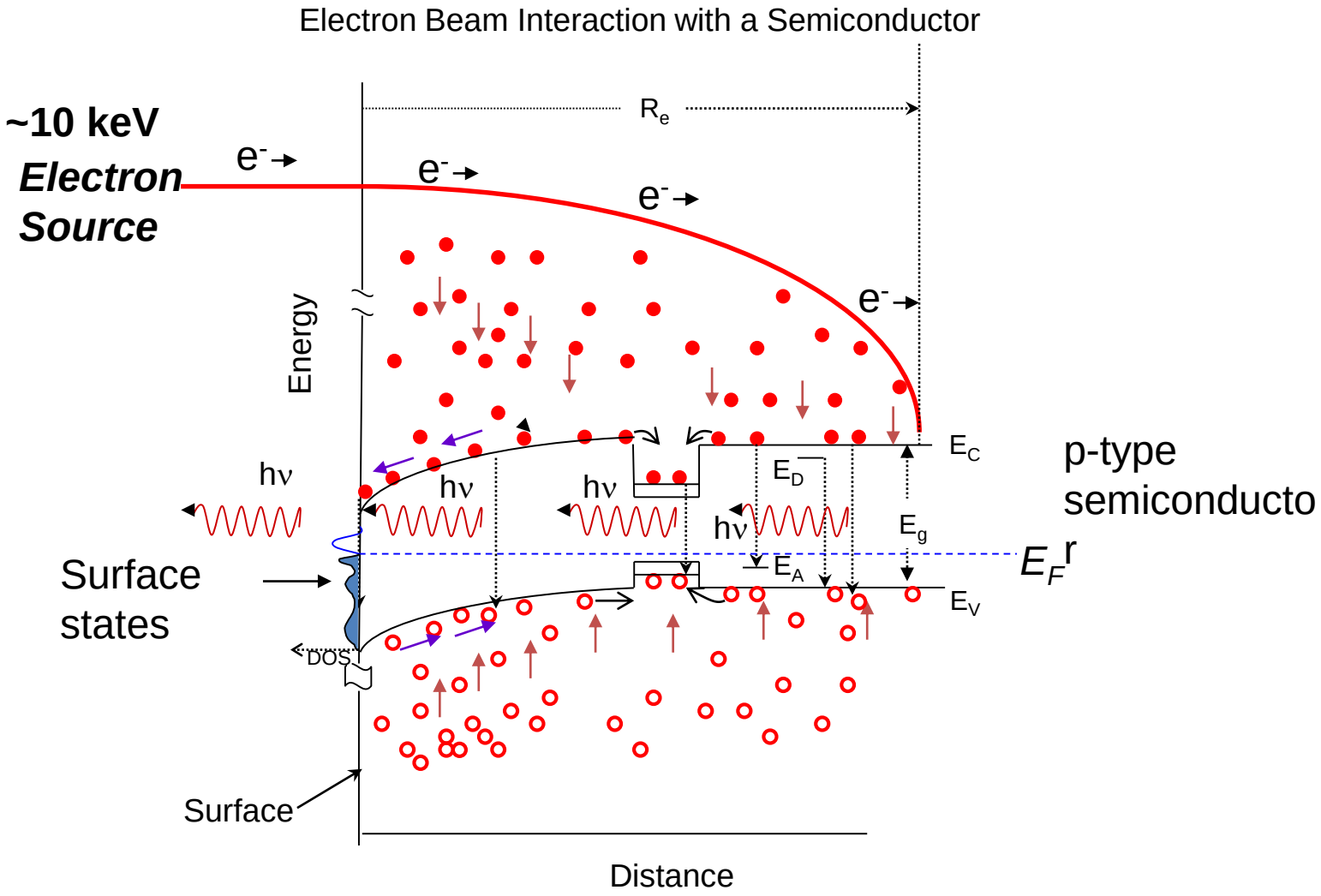
Flux of metal atoms



(Side view)

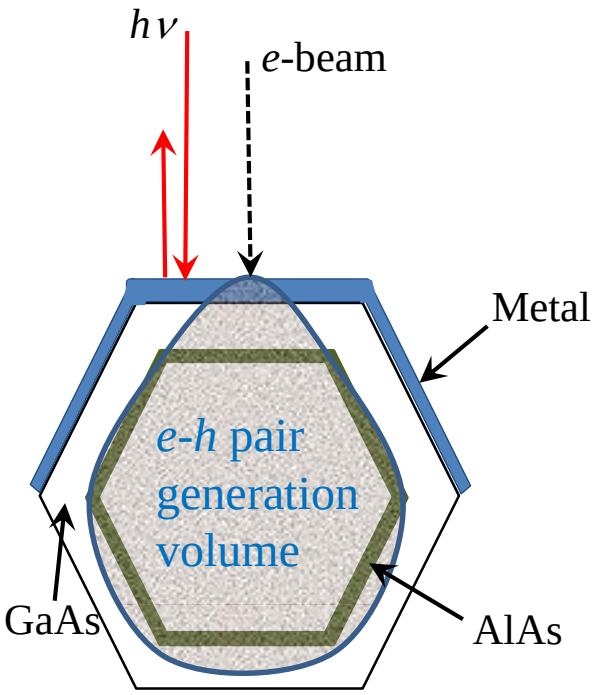
Tapered thickness or crescent shape in cross-section

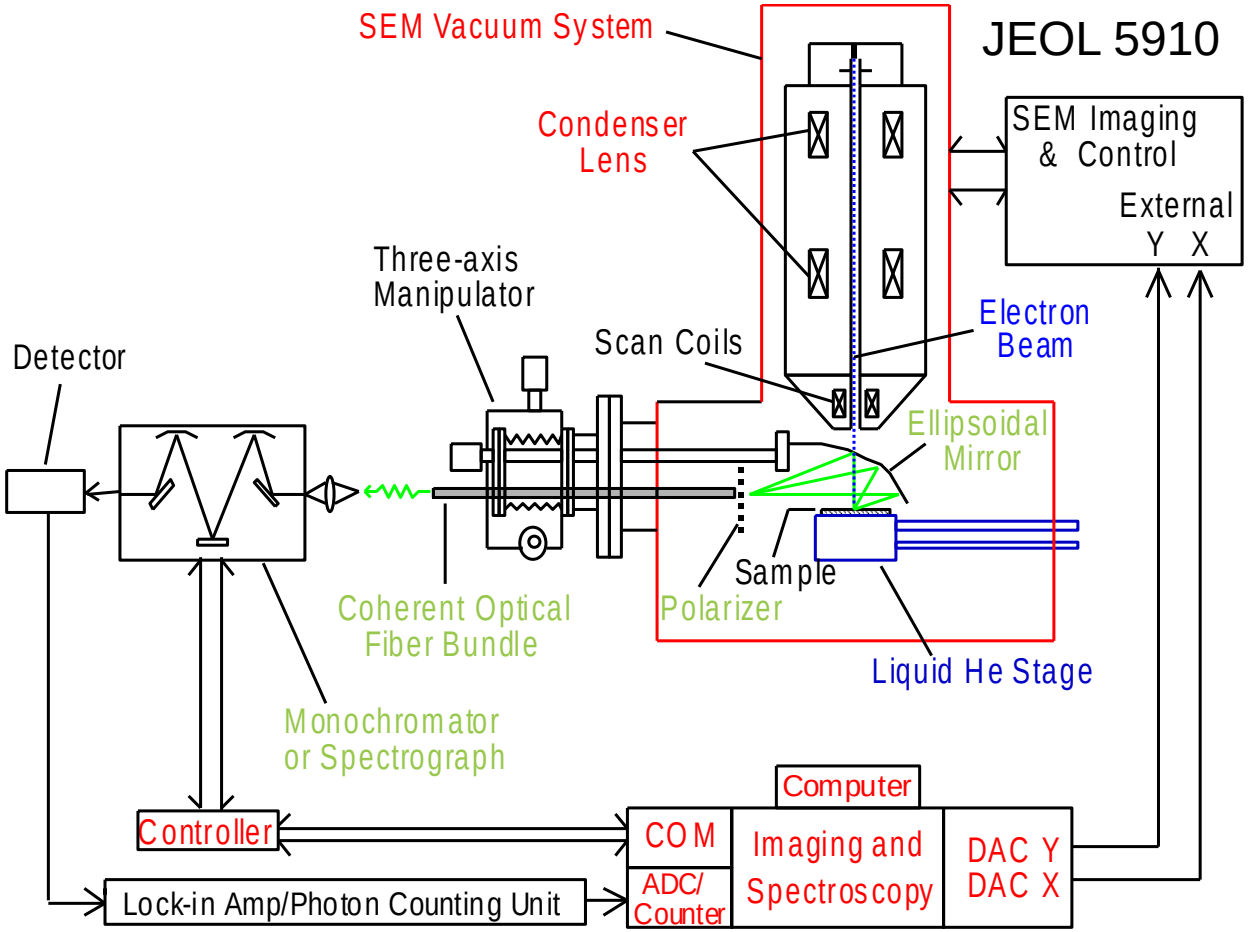
What is Cathodoluminescence (CL)?



Cathodoluminescence (CL) system

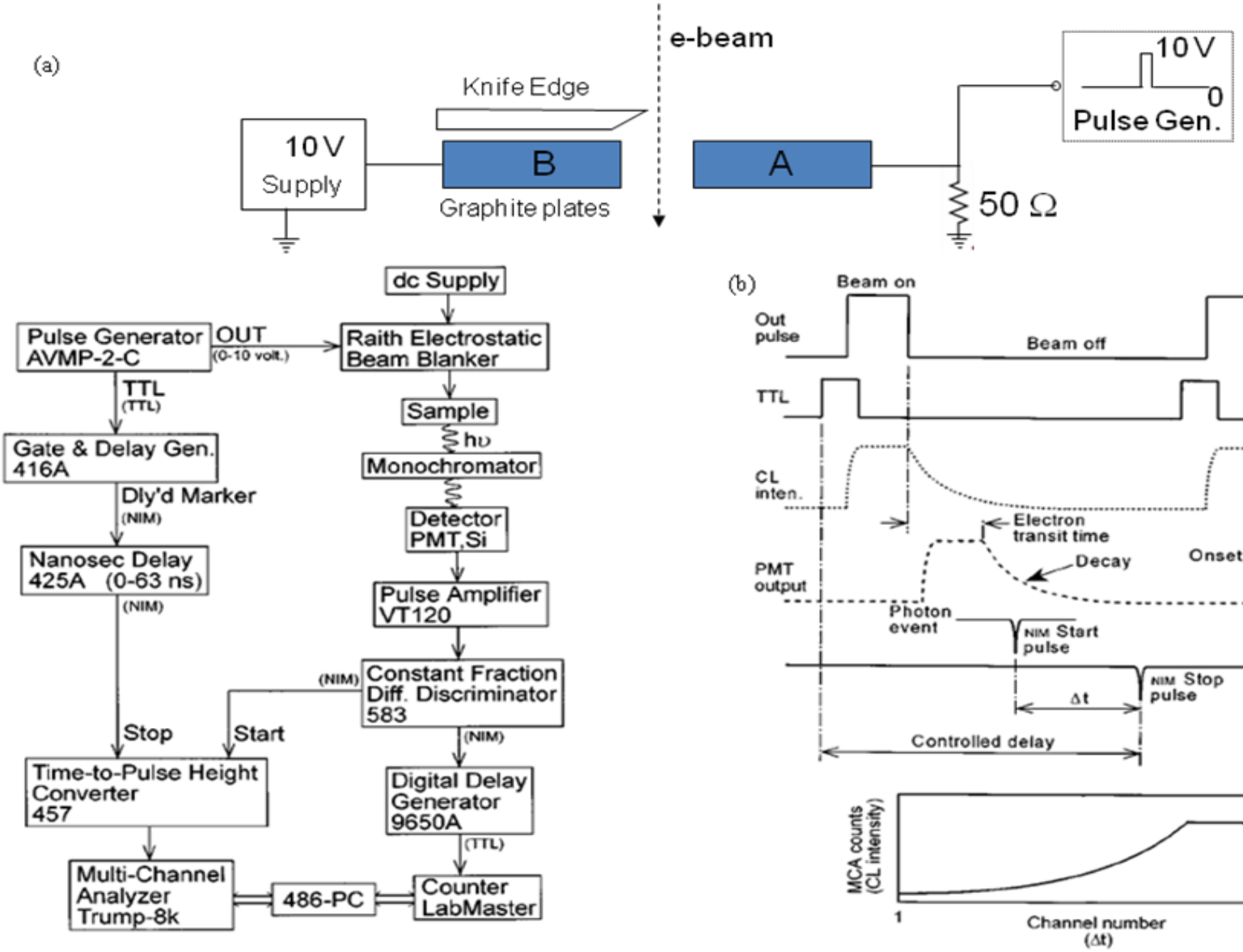
Advantage of *e*-beam over laser excitation for metal covered nanostructures:





Schematic diagram of optical collection system and data acquisition setup in our CL system.

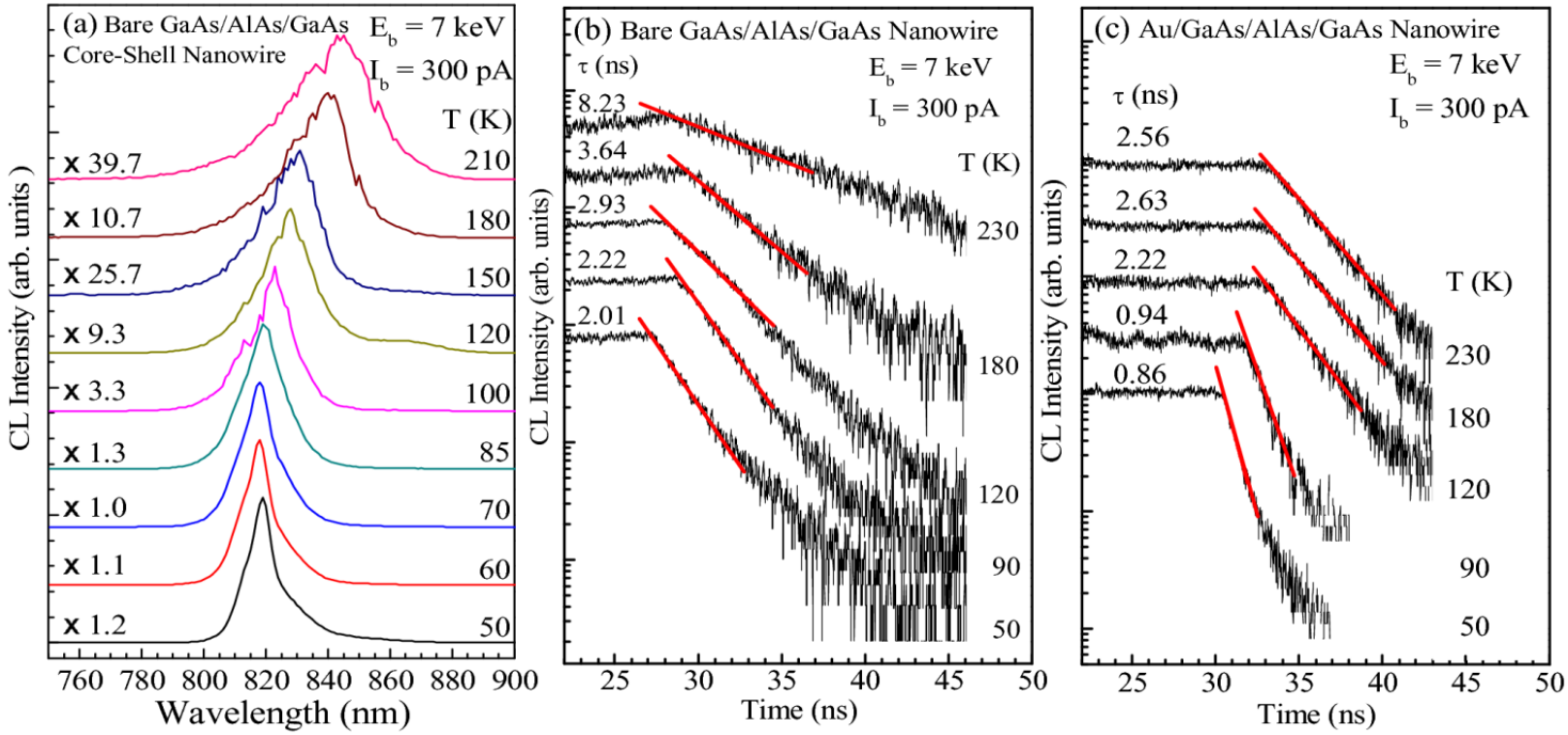
Time-resolved CL using time-correlated single photon counting



Instrumentation Block-diagram

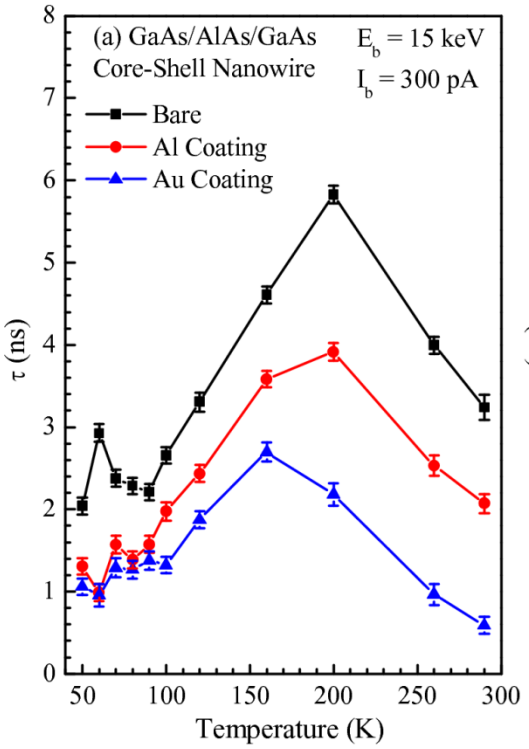
Method of delayed coincidence in an Inverted single photon counting mode

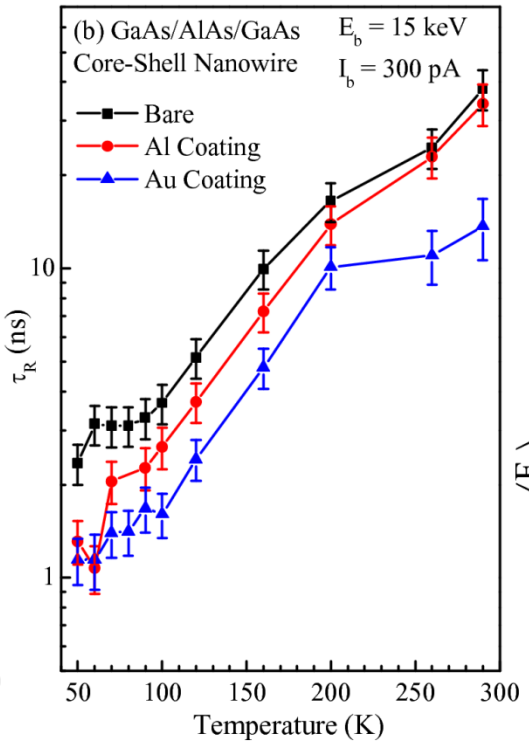
Temperature-dependent CL spectroscopy and time-resolved CL

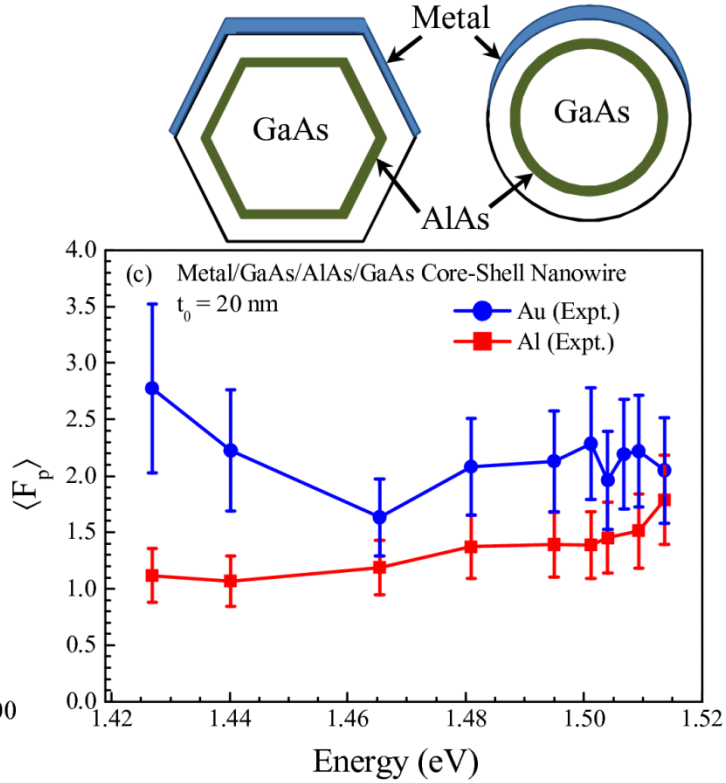


- GaAs NBE emission for *e*-beam excitation of a single nanowire (broadening, red-shift, and reduced intensity as *T* increases).
- Carrier lifetimes (τ) from slope of CL transients (single exponential fits).
- Deposition of Gold reduces τ at all temperatures relative to bare and Aluminum films.

Temperature dependence of $\tau_R(T)$ from $\tau(T)$ and the Purcell Factor (F_p)







We have extracted $\tau_R(T)$ from $\tau(T)$ and $I(T)$.

Radiative efficiency: $\eta(T) = \dfrac{\tau(T)}{\tau_R(T)} = \dfrac{I(T)}{I_0}$

I_0 is the saturation CL intensity at low temp.

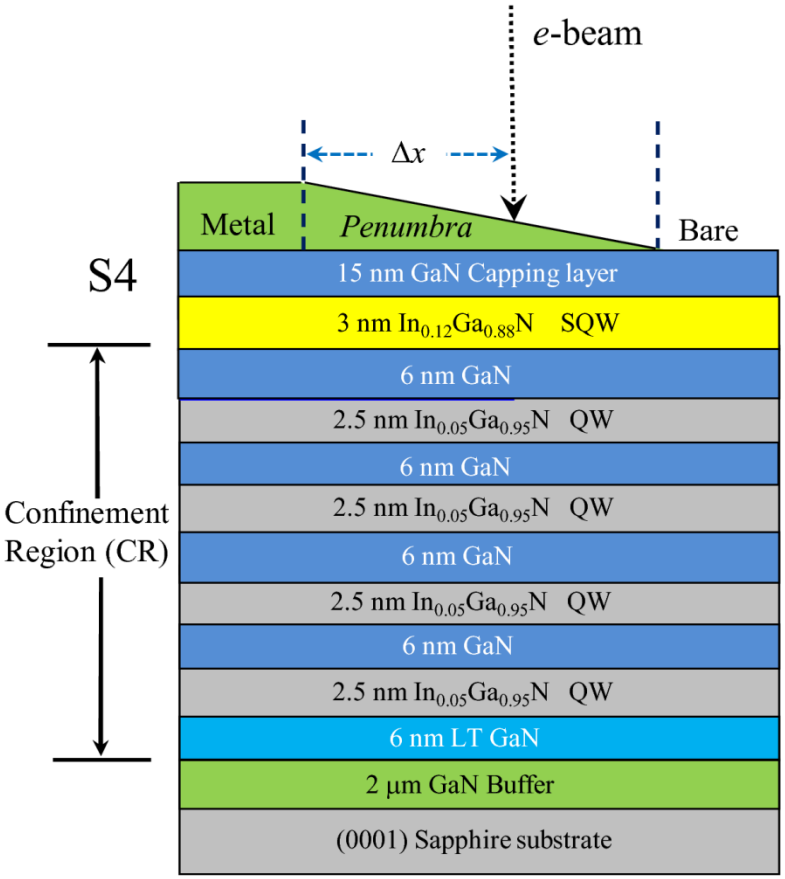
$\langle F_P(\omega) \rangle = \tau_{R(bare)} / \tau_{R(metal)}$

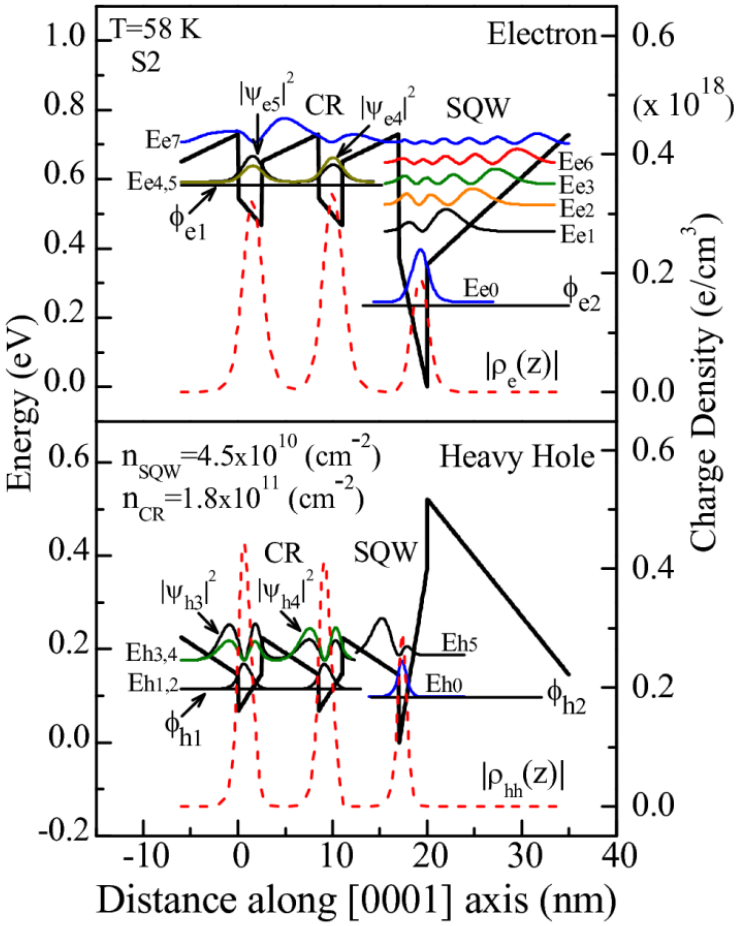
$\hbar\omega_{GaAs} \approx 1.510$ eV at $T = 50$ K
Au/GaAs: $\hbar\omega_{SP} \approx 1.804$ eV
Al/GaAs: $\hbar\omega_{SP} \approx 2.700$ eV
(From ω vs k dispersion calculation)
Therefore, we expect F_p (Au) > F_p (Al)

Time-resolved CL and CL imaging of InGaN/GaN QWs with metal films for exciton-to-SPP coupling

MOCVD-grown In_xGa_{1-x}/GaN MQW Samples

Metal films: Ag, Au, and Al, thickness of 20 nm





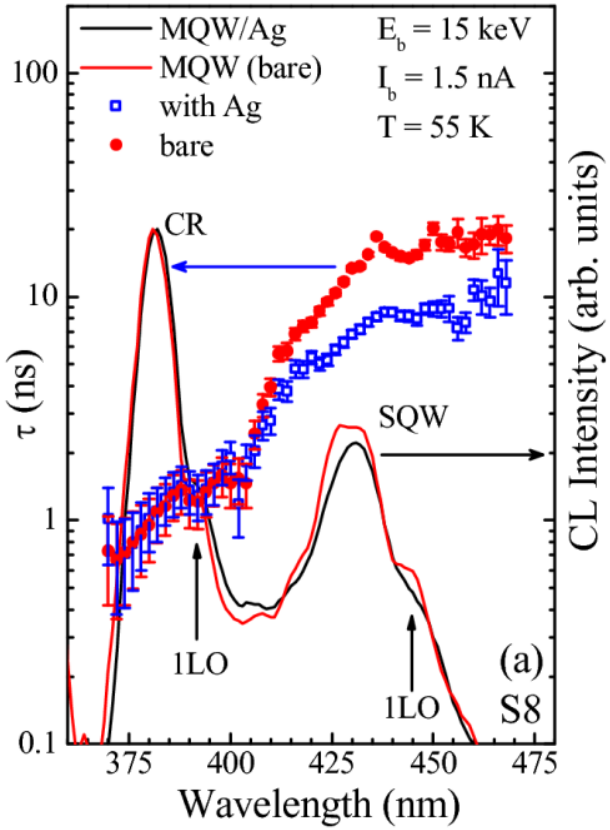
Calculation of Energy states and wavefunctions for confined electrons and holes:

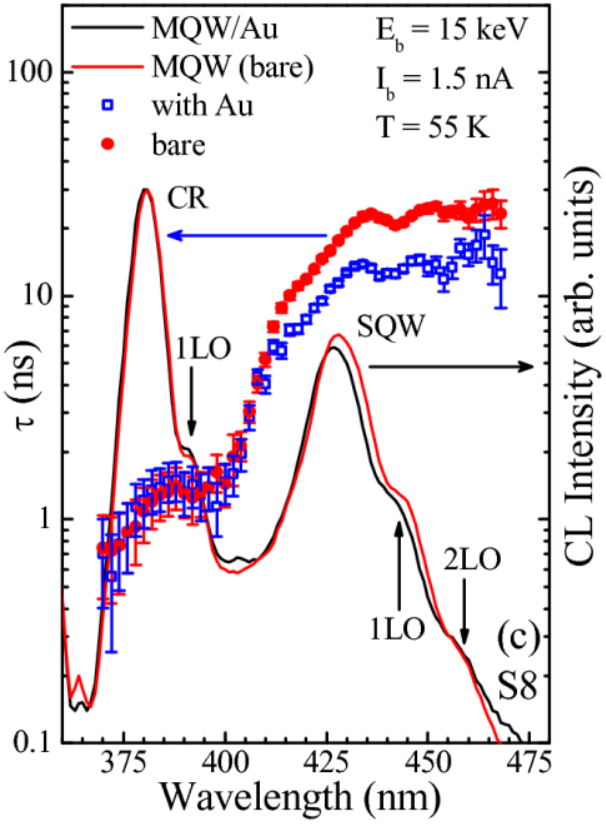
E-field and confinement potential are different for SQW and CR regions.

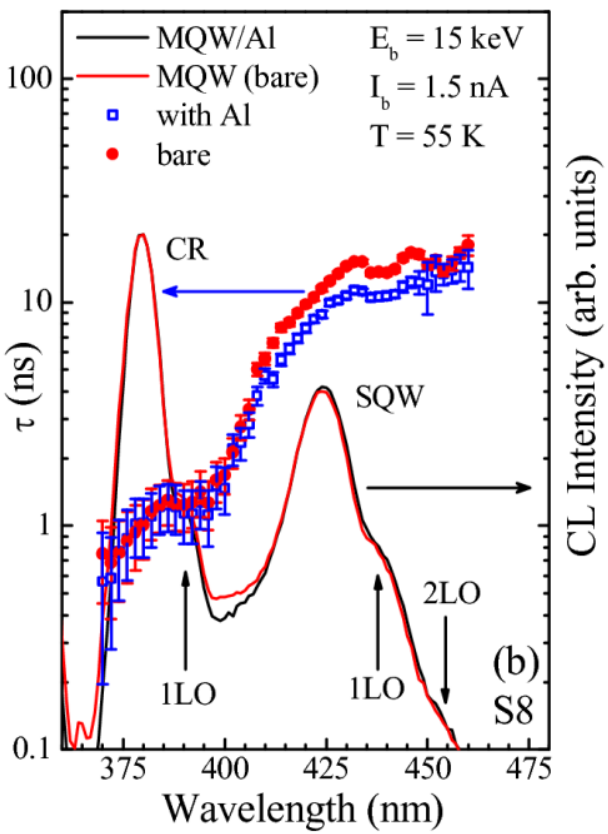
Time-resolved CL of bare and metal-coated InGaN/GaN QWs

MOCVD-grown In_xGa_{1-x}/GaN MQW Samples

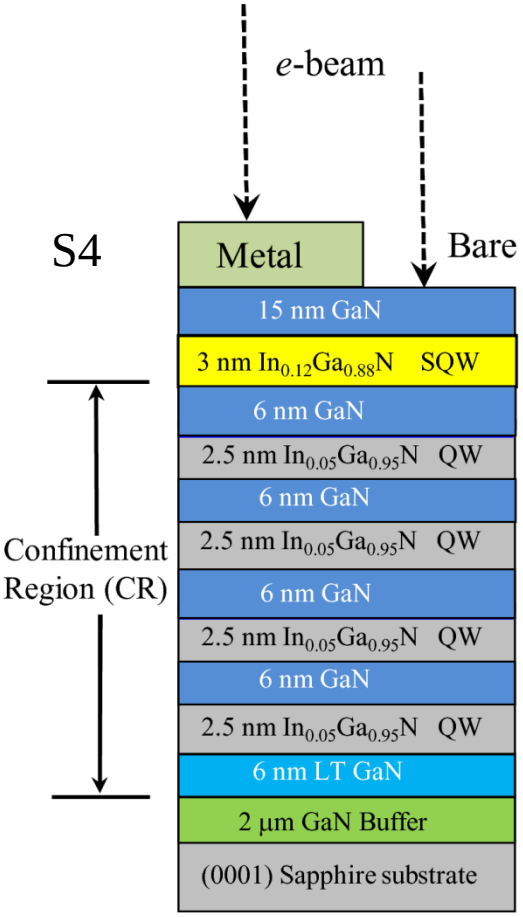
Metal film: Ag, Au, and Al, thickness of 20 nm
Defocused *e*-beam area: ~1500 μm²



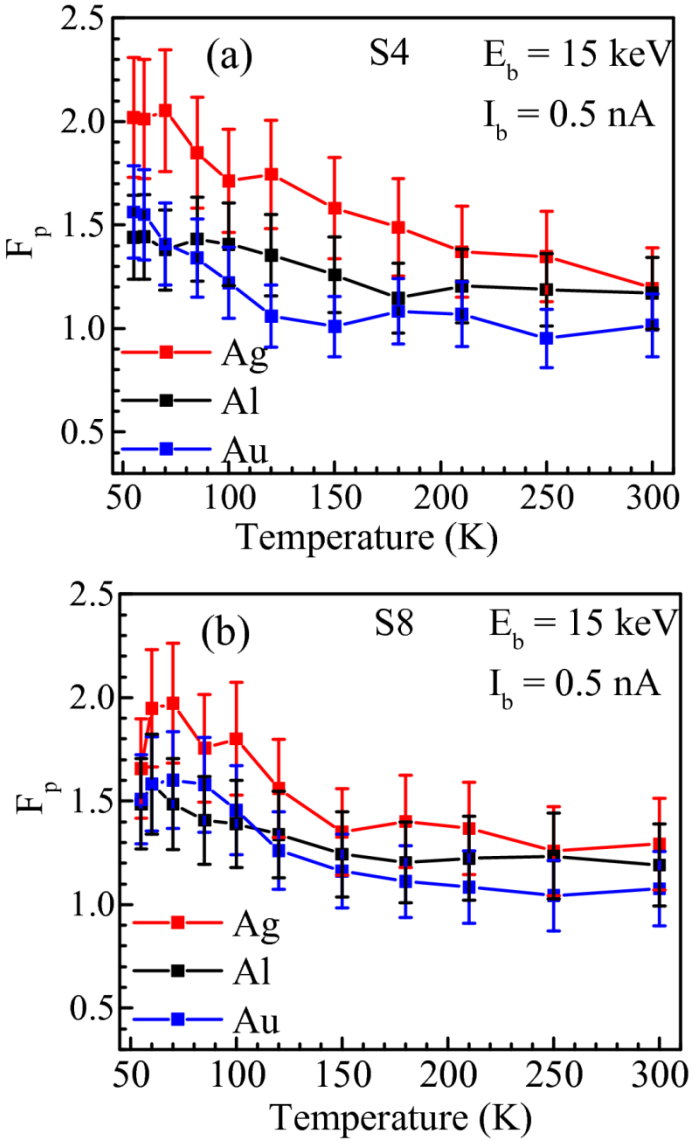




Temperature Dependence of the Purcell Factor (F_P) for the InGaN/GaN SQW



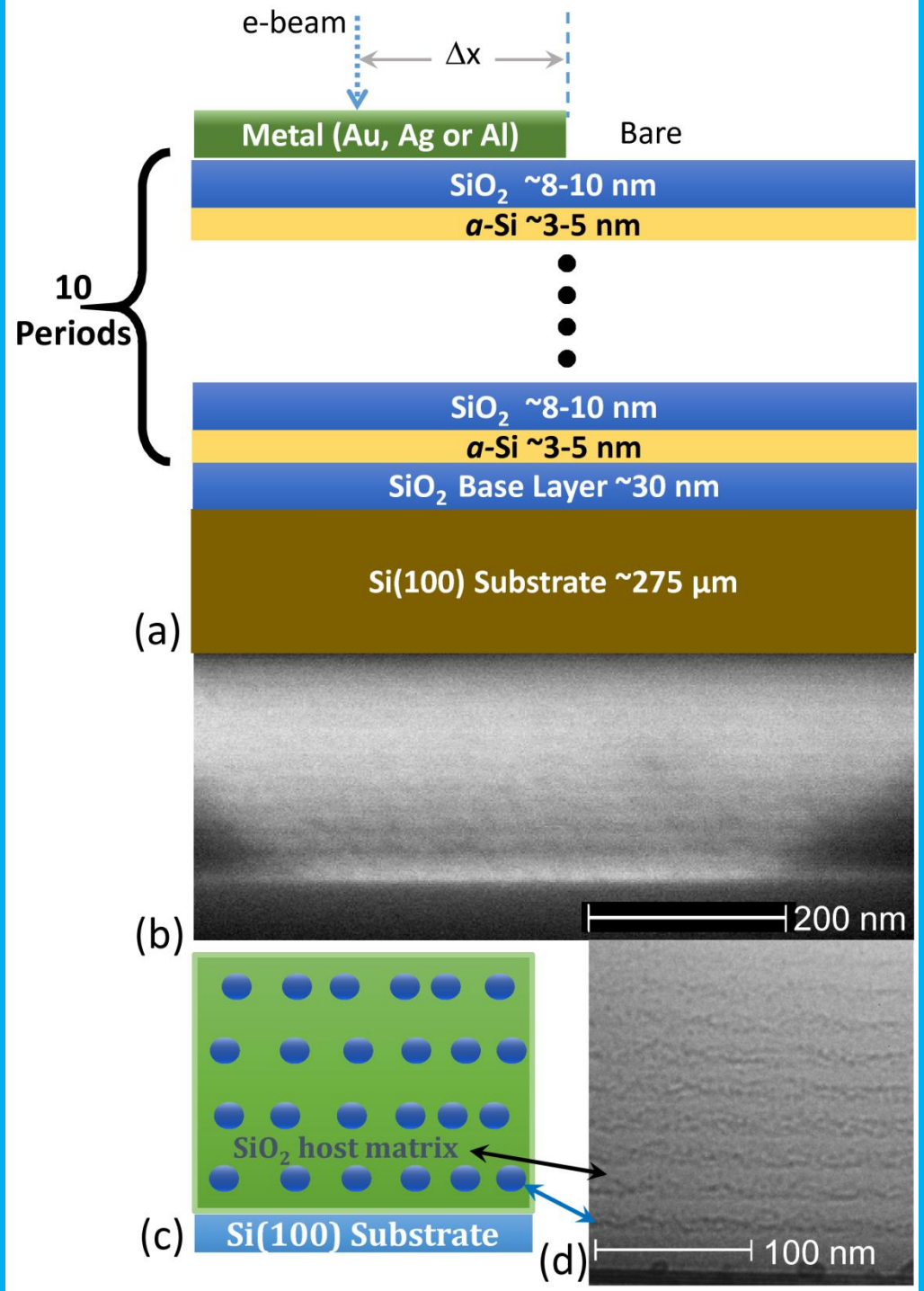
S4 – 4 QWs in the CR
S8 – 8 QWs in the CR



$$F_P(T) = \tau_{R(bare)} / \tau_{R(metal)}$$

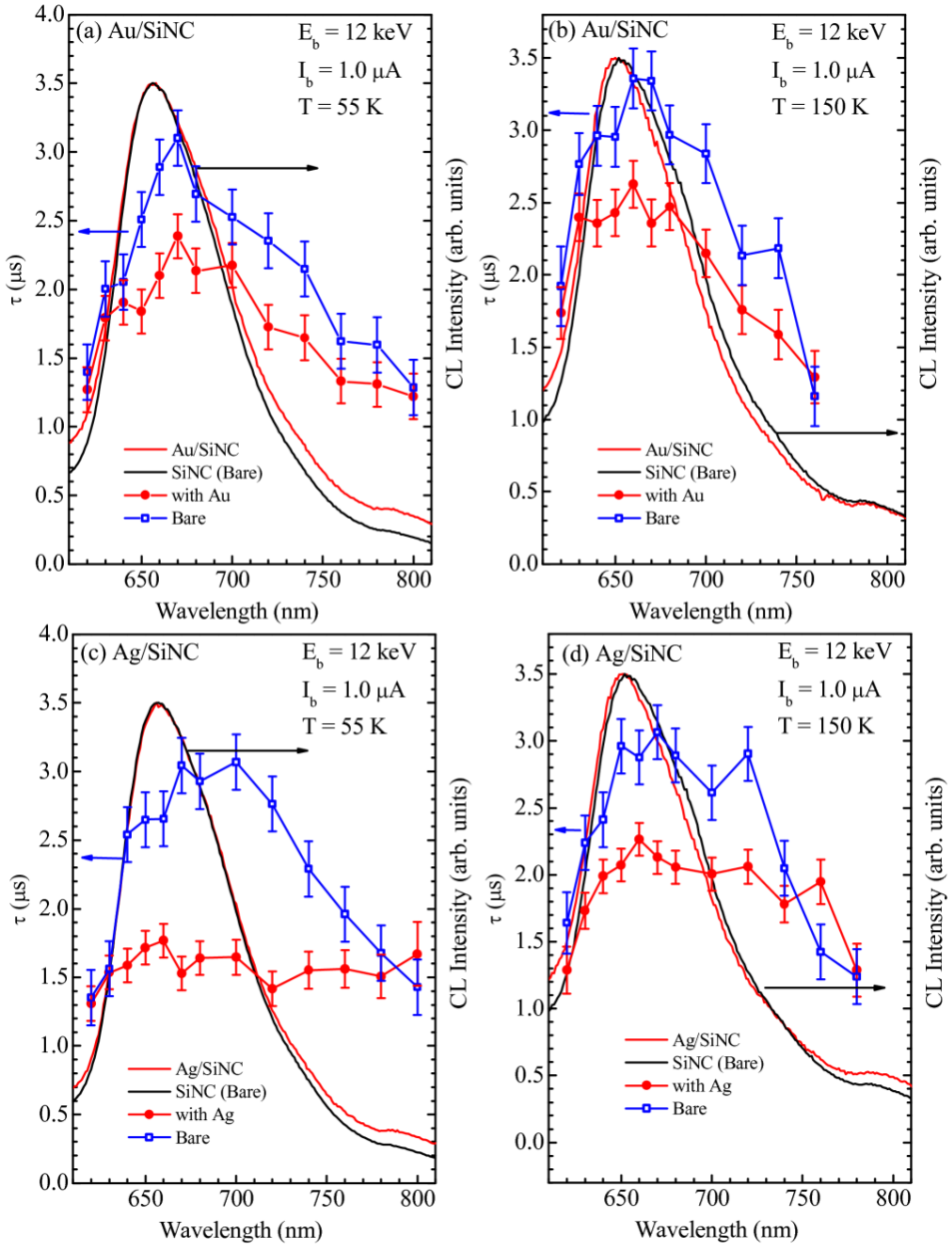
The Ag film yields the largest F_p, followed by Al and Au.

Losses in the metal likely cause decrease in F_p as temp. increases.



Enhancement in the excitonic spontaneous emission rates for Si nanocrystal (SiNC) multi-layers covered with thin films of Au, Ag, and Al

- The radiative decay rates of SiNCs are relatively small (lifetimes, τ, of ~10^{-6} to 10^{-3} s) compared to III-V NCs ($\tau \sim 10^{-9}$ s).
- Compatibility with current Si microelectronics technology, Si LED would lead to optical interconnection applications in various stages of integrated-circuit fabrication.
- SiNCs were grown using plasma enhanced chemical vapor deposition (PECVD). Amorphous silicon (*a*-Si) and SiO_2 thin films were deposited on top of commercial Si(100) wafers . The *as-grown multi-layer* sample was annealed at 1150°C for 1 hour in a N_2 flow chamber: *a*-Si → SiNCs



The wavelength dependence of the lifetime (τ) for Au and Ag films on the SiNC sample.

Plots of τ vs λ are superimposed on plots of the CL spectra for the bare and metal-covered sample. The results are shown for temperatures of 55 and 150 K.

The peaks of the lifetime plot are shifted ~10 nm (~30 meV) towards larger λ for temperatures of 55 and 150 K, consistent with a reduced oscillator strength for larger SiNCs within the ensemble.

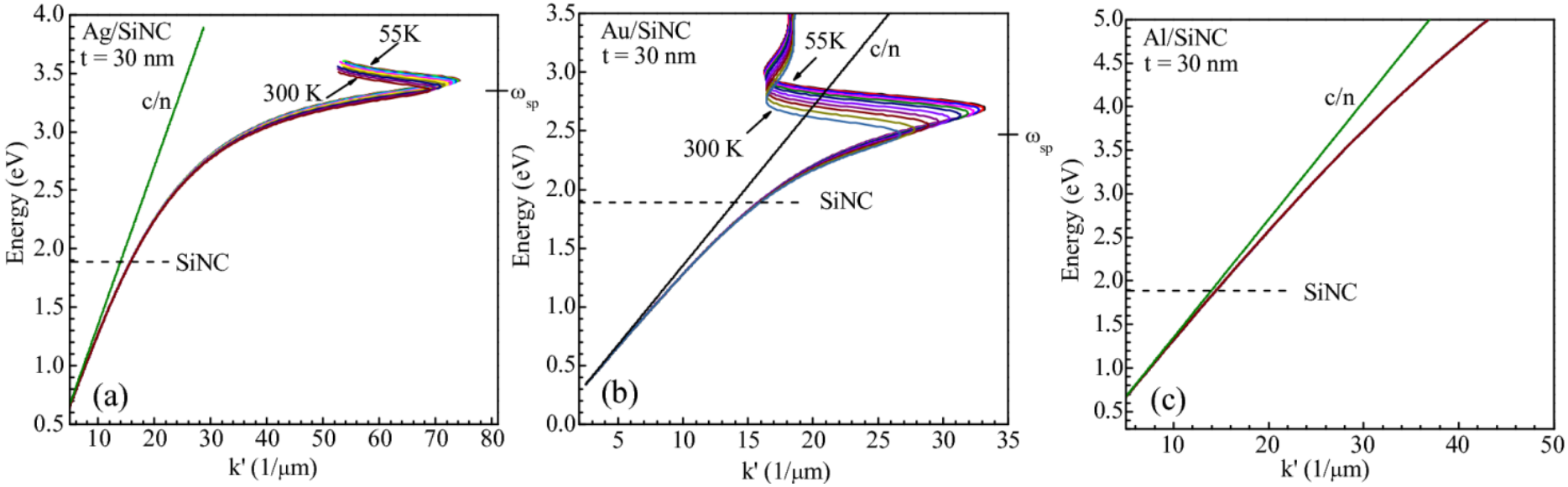
The maximum ratio (r) of the lifetimes, for which $r = \tau_{(bare)}/\tau_{(metal)}$, is ~1.4 and 2.0 at T = 55 K for the Au and Ag covered samples, respectively . Related to the energy difference between SiNC emission and ω_{sp}.

The calculated ω vs k' SPP dispersion relations for metal/SiO2/SiNC

The method is the same as used for metal/GaN/InGaN with different ε(ω, T) for SiO_2

$$\varepsilon(\omega,T)=\varepsilon_{\infty}-\frac{\omega_p(T)}{\omega^2+i\omega\gamma(T)}+\varepsilon_{CP1}(\omega,T)+\varepsilon_{CP2}(\omega,T)$$

For Au and Ag, as before.



Numerical solutions to the dispersion relation:

$$\left(\frac{k_{zd}}{\varepsilon_d}+\frac{k_{zm}}{\varepsilon_m}\right)\left(\frac{k_{air}}{\varepsilon_{air}}+\frac{k_{zm}}{\varepsilon_m}\right)-\left(\frac{k_{zd}}{\varepsilon_d}-\frac{k_{zm}}{\varepsilon_m}\right)\left(\frac{k_{air}}{\varepsilon_{air}}-\frac{k_{zm}}{\varepsilon_m}\right)\exp\left(-2k_{zm}h\right)=0$$

$$k_{zair}^2=k_x^2-\frac{\omega^2}{c^2}\varepsilon_{air},\quad k_{zm}^2=k_x^2-\frac{\omega^2}{c^2}\varepsilon_m,\quad k_{zd}^2=k_x^2-\frac{\omega^2}{c^2}\varepsilon_d$$

$$F_p(\omega,z)=1+\frac{\pi c^3\left|E(z)\right|^2}{4\omega^2\int_{-\infty}^{+\infty}u_E(\omega,z')dz'}\rho_{2D}(\omega),\qquad \rho_{2D}(\omega)=\frac{1}{4\pi}\frac{\partial k^2}{\partial\omega}$$

from Fermi's Golden rule; Phys. Rev. B **60**, 11564 (1999).

For a dielectric in the transparency region (i.e., $|\varepsilon''(\omega)| << |\varepsilon'(\omega)|$) the energy density of the electric field in the layer is given by

$$u_E(\omega,z)=\frac{1}{8\pi}\left[\frac{\partial(\omega\varepsilon')}{\partial\omega}\right]\left|E(z)\right|^2$$

However, for metals with dissipation, the expression for the energy density is

$$u_E(\omega,z)=\frac{1}{8\pi}\left[\varepsilon'+\frac{2\omega\varepsilon''}{\gamma}\right]\left|E(z)\right|^2$$

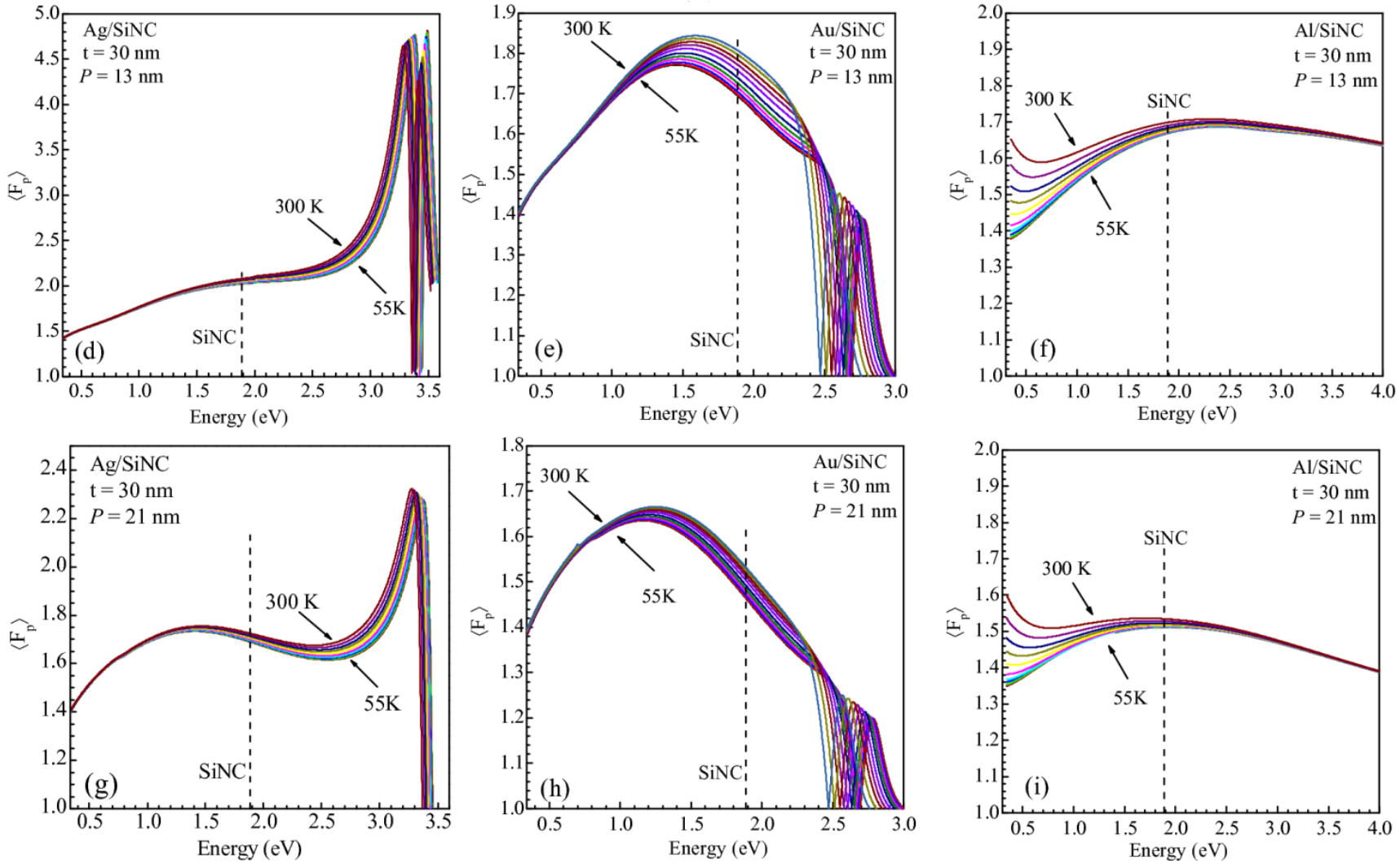
γ is the damping constant from the Drude model.

$$F_p(\omega,z)=1+\frac{\pi c^3\exp\left(-2k_{z3}z\right)}{\omega^2\left[\frac{\exp\left(-2k_{z2}t\right)}{k_{z1}}+\left(\varepsilon_2'+\frac{2\omega\varepsilon_2''}{\gamma}\right)\left(\frac{1-\exp\left(-2k_{z2}t\right)}{k_{z2}}\right)+\frac{\partial(\omega\varepsilon_3')}{\partial\omega}\frac{1}{k_{z3}}\right]}\frac{\partial\left(k^2\right)}{\partial\omega}$$

i = 1 to 3 represent the vacuum, metal, and GaAs regions.

The calculated Average Purcell Factors $\langle F_p \rangle$ metal/SiO_2/SiNC

- $\langle F_p \rangle$ is the average of F_p over the 10-period SiO_2/SiNC structure.
- The calculations were performed for two different periodicities (P) of 13 and 21 nm.
- $\langle F_p \rangle$ is remarkably consistent with the experimental results for $r = \tau_{(bare)}/\tau_{(metal)}$, which are ~1.4 and 2.0 at T = 55 K for the Au and Ag films.



Summary

- The coupling of excitons to surface plasmon polaritons (SPPs) in metal films on GaAs/AlAs/GaAs core-shell nanowires, InGaN/GaN QWs, and Si Nano-crystals was probed using time-resolved cathodoluminescence (CL).
- Excitons were generated in the metal-coated nanostructures and QWs by injecting a pulsed high-energy electron beam through the thin metal films.
- The average Purcell enhancement factor, $\langle F_P \rangle$, was obtained by the direct measurement of the changes in the integrated NBE CL emission intensities and the temperature-dependent lifetimes.
- A model was presented for $\langle F_P \rangle$ for the three material systems, which takes into account the effects of ohmic losses of the metals and changes in the dielectric properties due to the temperature dependence of (*i*) the intraband behavior in the Drude model and (*ii*) the interband critical point transition energies which involve the *d*-bands of Au and Ag.

Additional information is found in our papers on this subject:

1. Y. Estrin, D. H. Rich, A. V. Kretinin, and H. Shtrikman, *Nano Letters* **13** (4), pp. 1602–1610 (2013).

2. Y. Estrin, D. H. Rich, S. Keller, and S. P. DenBaars, *Journal of Applied Physics* **117**, 043105, pp. 1-14, (2015).

3. Y. Estrin, D. H. Rich, S. Keller, and S. P. DenBaars, *Journal of Physics*: *Condensed Matter* **27**, 265802, pp. 1-13, (2015).

4. Y. Estrin, D. H. Rich, N. Rozenfeld, N. Arad-Vosk, A. Ron, and A. Sa'ar, *Nanotechnology* **26**, 435701 (2015).