Modification of emission properties of ZnO layers due to plasmonic near-field coupling to self-organized Ag nanoislands

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Plan

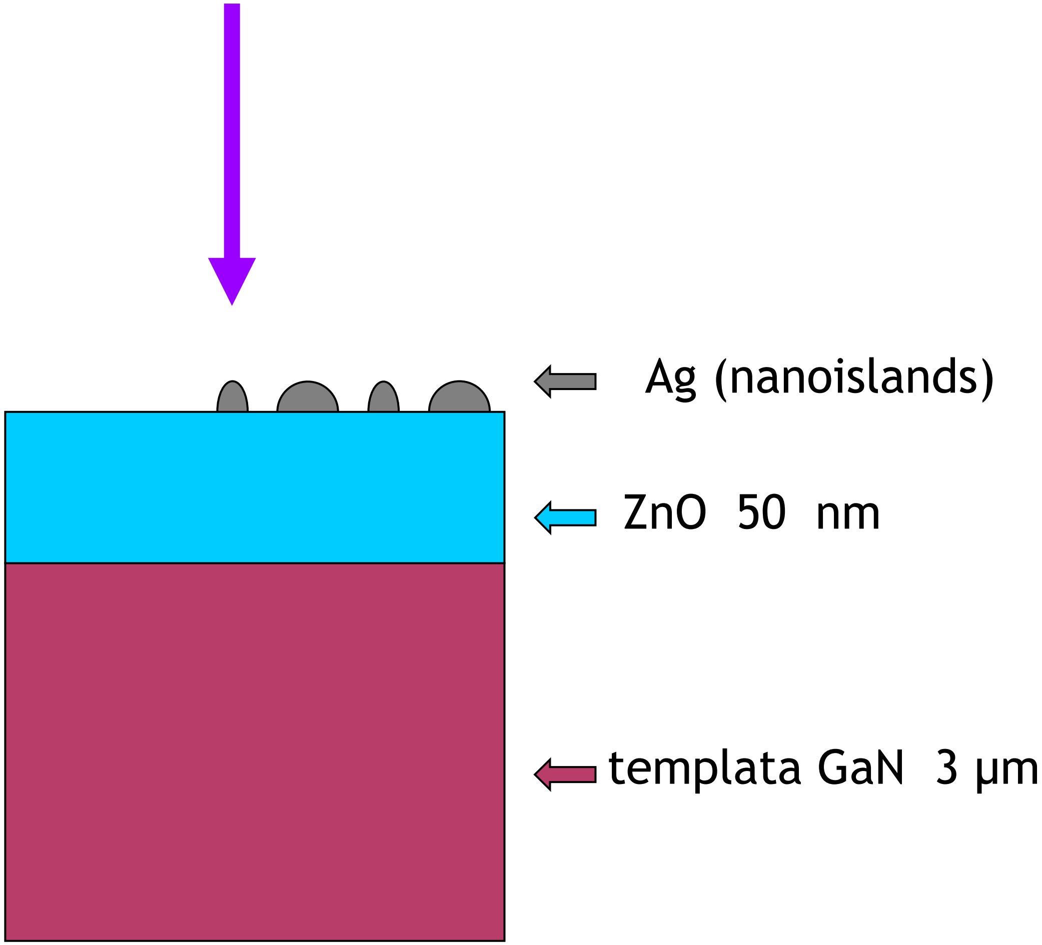
plasmonic self-organized Ag nanoislands

1. Samples
2. Scanning electron microscope (SEM)
3. Experiment
4. Photoluminescence (PL)
5. Time-resolved PL (TRPL)
6. Theoretical model
7. Conclusions
8. Plan

Samples ZnO

- **sample A:**
covered with silver islands by sputter deposition lasting for 2 s

- **sample B:**
coated by Ag sputtering over 15-20 s, yielding a 3 nm layer of Ag, and then annealed at temperature of 750°C for 3 min

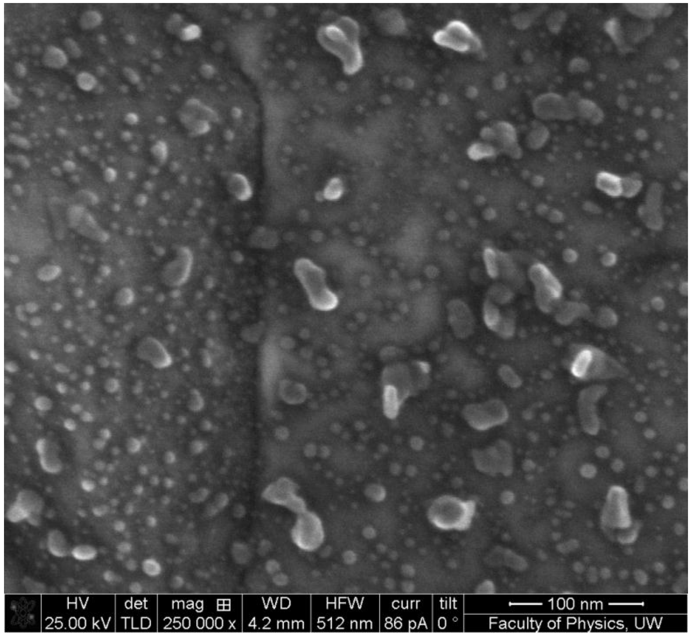


atomic layer deposition (ALD) method

B. Witkowski IF PAN

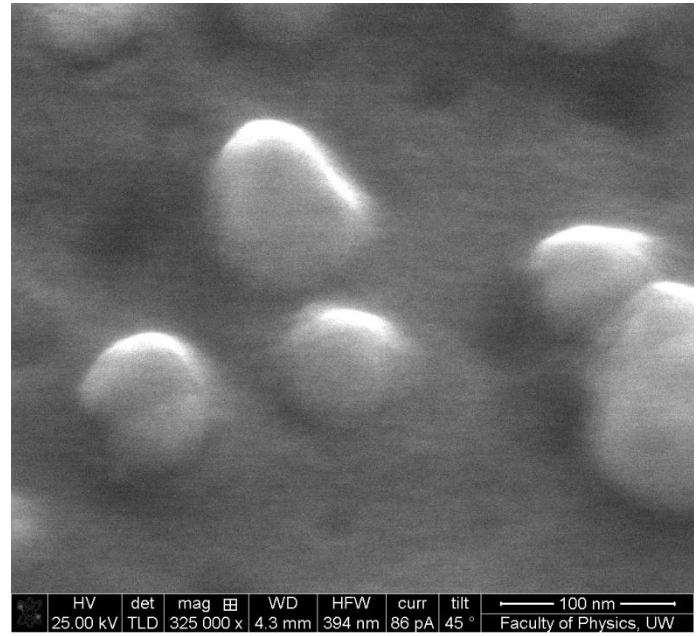
Scanning Electron Microscope (SEM)

Sample A



diameter D = 10-40 nm
surface density $\rho \approx 2000/\mu m^2$

Sample B



diameter D = 70-100 nm
surface density $\rho \approx 25/\mu m^2$

The Ag islands have a quasi-spherical shape in both samples.

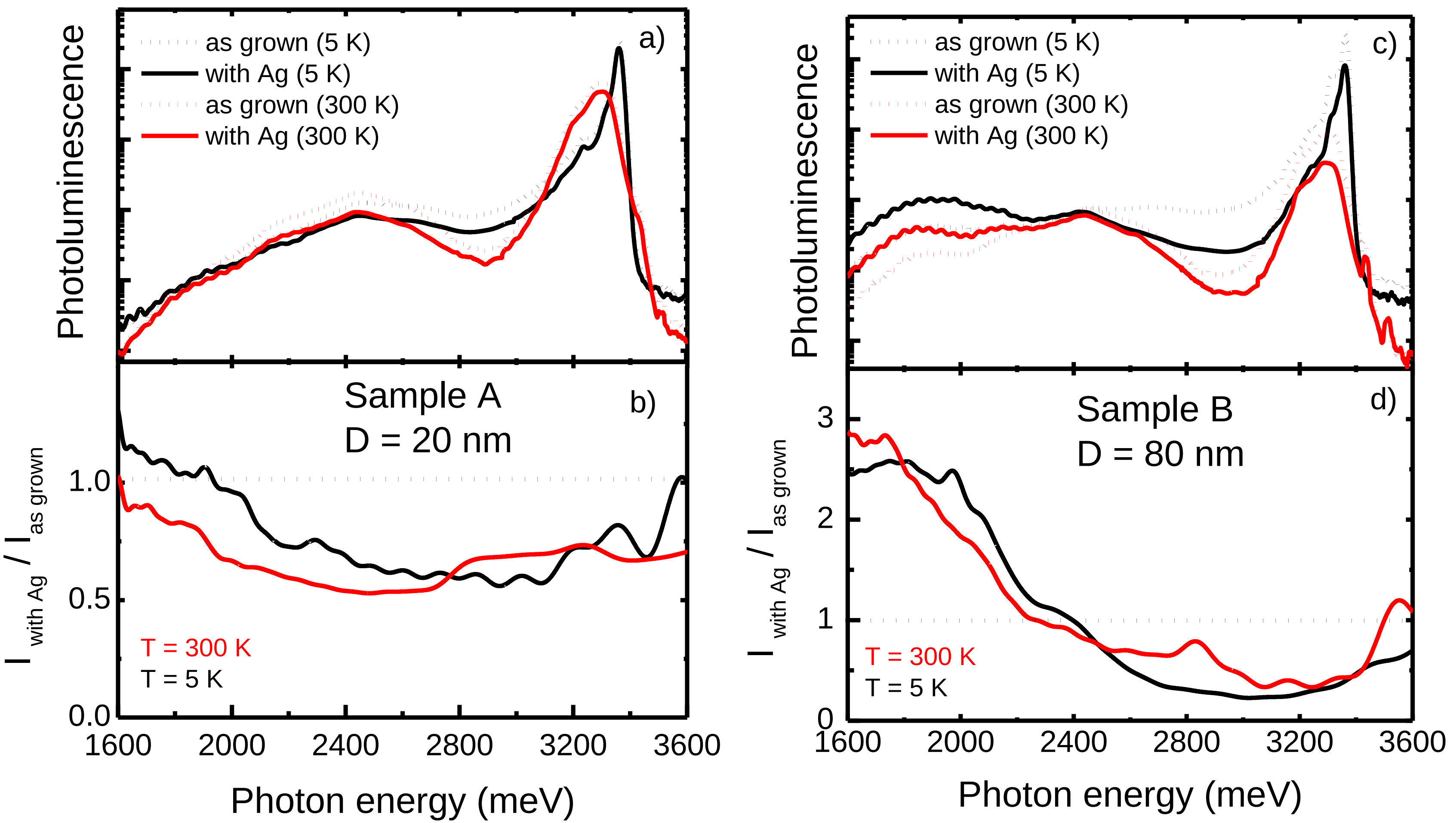
Experiment

- **Photoluminescence (PL)**
  - emission excited at 325 nm (3.81eV) (He-Cd laser)
  - at 5 K and 300 K
  - a grating monochromator (600 gr/mm or 1800 gr/mm)
  - CCD camera

- **Time-Resolved PL (TRPL)**
  - emission excited at 300 nm (4.1eV) (frequency tripled Ti:Sapp pulsed laser)
  - at 4 K
  - a grating monochromator (600 gr/mm or 1800 gr/mm)
  - a streak camera

- **Transmission**
  - a halogen lamp as the light source
  - at 300 K
  - a grating monochromator (600 gr/mm or 1800 gr/mm)
  - CCD camera

PL spectra



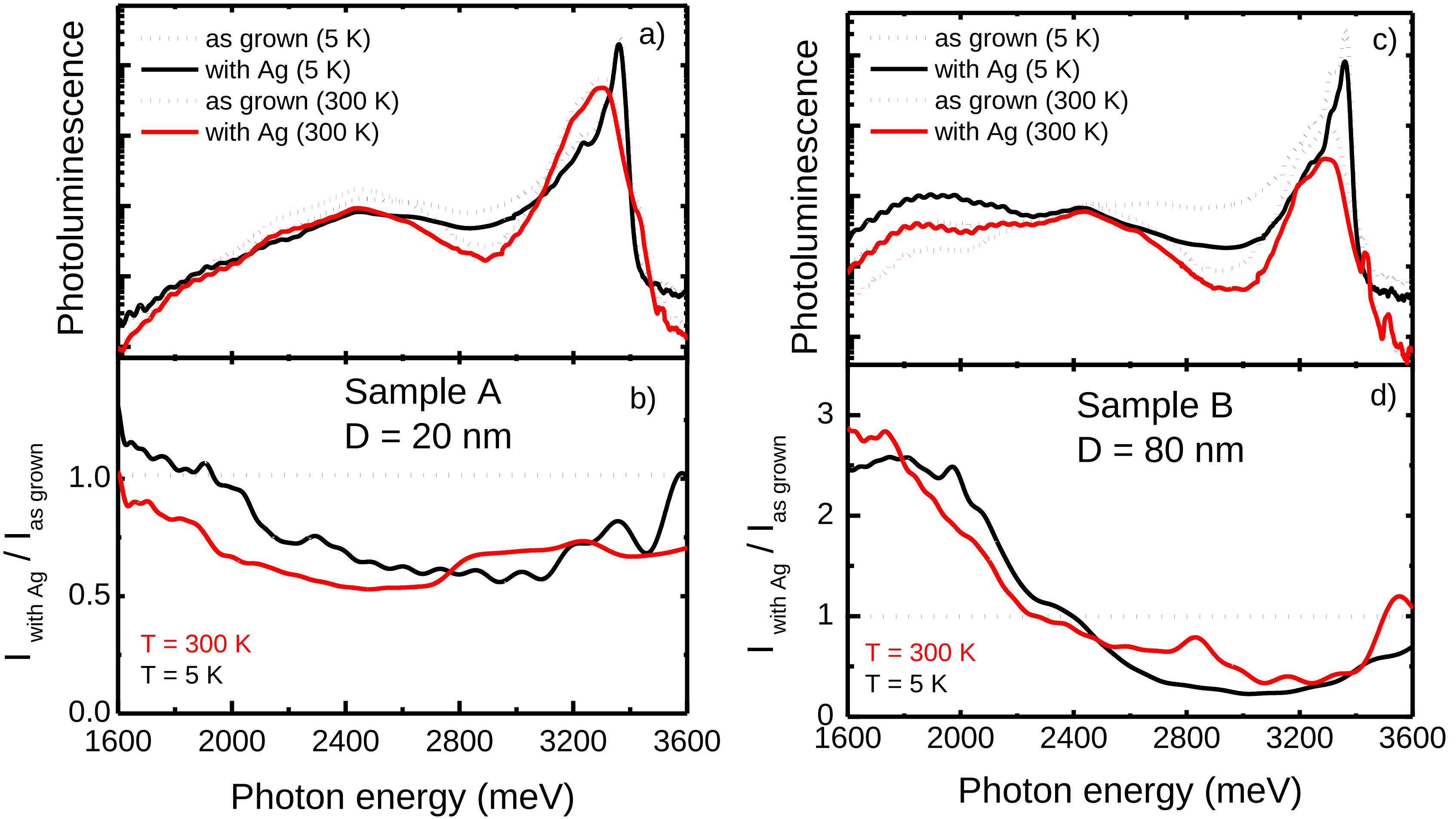
➢ optical transitions:

✓ ~3.36 eV → bound exciton emission in ZnO

✓ 2.90-3.33 eV → stacking faults

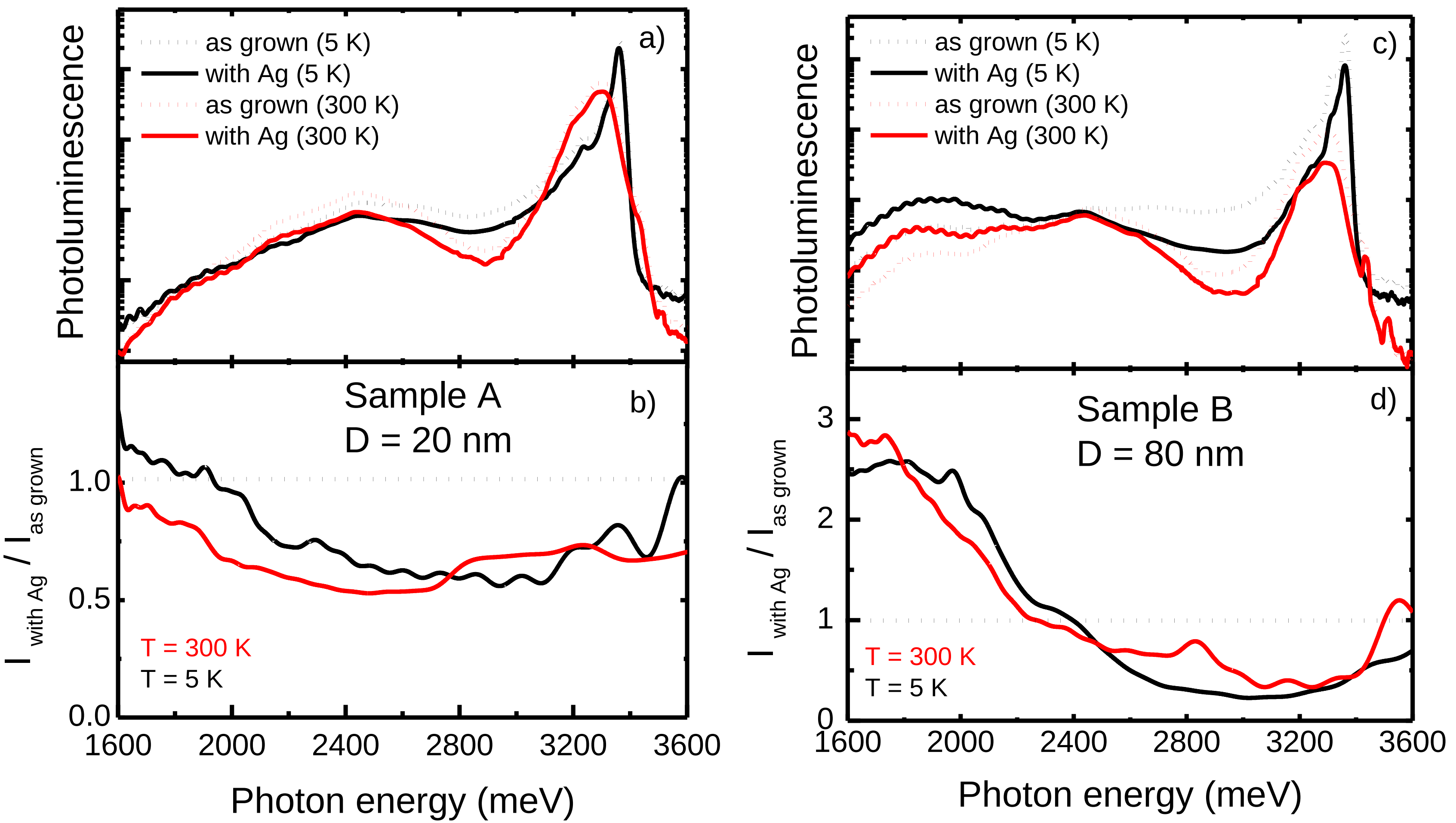
✓ below ~2.9 eV → a weak defect

➢ temperature increase → a shift towards lower energies and broadening



- ➢ sample A (10-20 nm Ag islands)
- ✓ slight PL decrease in the almost entire spectral range

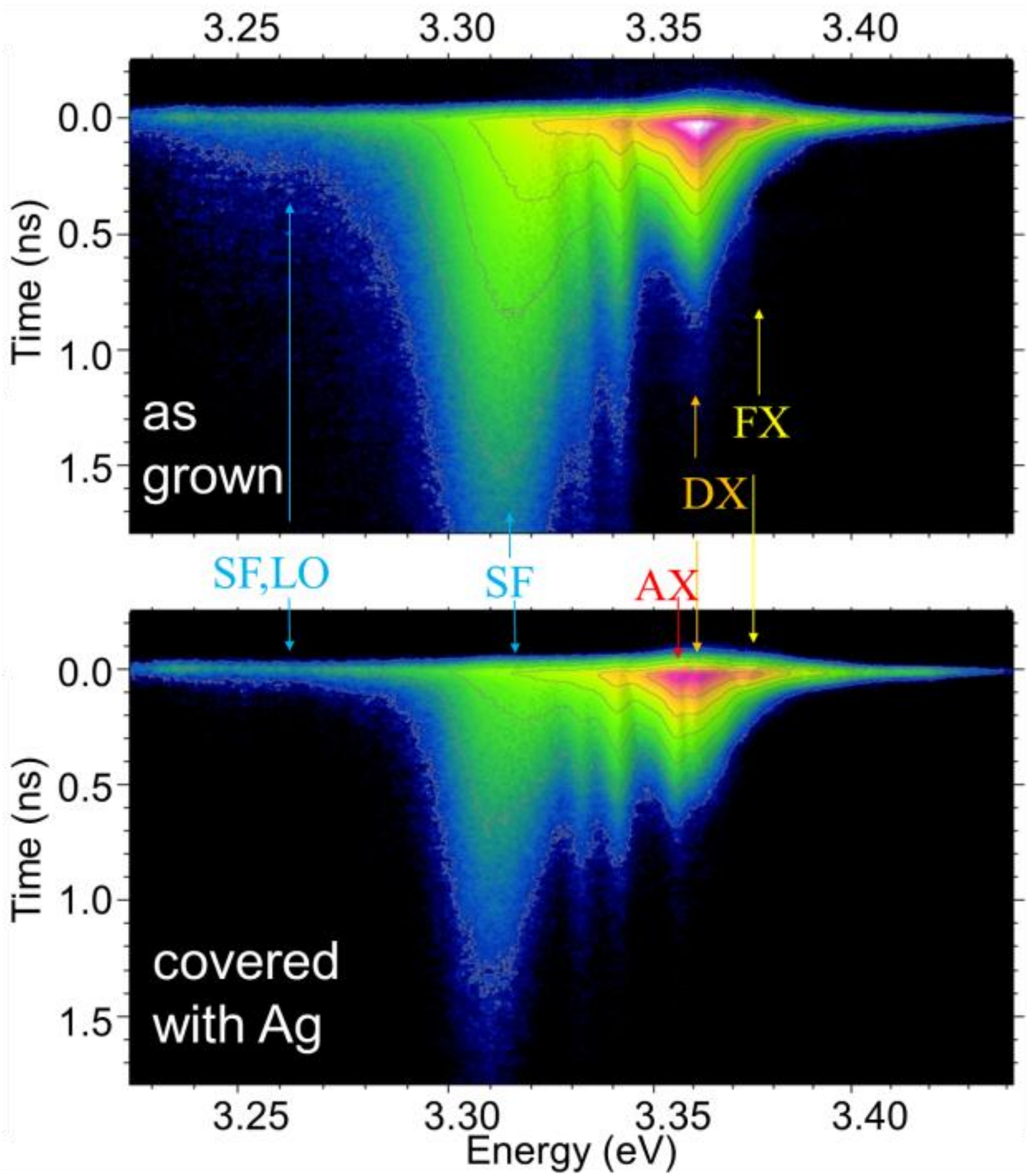
- ➢ sample B : (80-90 nm Ag islands)
- ✓ enhancement of the emission → below ~2.4 eV
- ✓ a quenching of the emission → above ~2.4 eV



enhancement or quenching are independent of temperature & magnitude of electron density independent of temperature → plasmonic effects in Ag

PL spectra

Sample B



Transmission:

- free exciton (**FX**) → 3.375 eV
- donor bound exciton (**DX**) → 3.361 eV
- two weak peaks → 3.33 eV and 3.34 eV
- stacking fault (**SF**) → 3.30 – 3.33 eV
- acceptor bound exciton (**AX**) → 3.356 eV (not observed in the signal from the uncovered sample) → the diffusion of the Ag atoms, acting as acceptor centers, to ZnO layer during the process of the sample annealing

Time-Resolved PL

Time-Resolved PL

Transition		FX	DX	SF
Energy (eV)		3.375	3.36	3.30 - 3.33
PL lifetime (ps) (fast components)	as grown	35(5)	77(5)	40(15)
	with Ag	25(5)	66(5)	30(10)
Intensity (10^3 counts)	as grown	4.7	39	7.0
	with Ag	4.0	17	1.3

- large Ag nanoislands → reduced decay times and emission intensity → the existence of additional nonradiative channel related to the coupling of the emission to surface plasmons confined in the Ag nanoislands

- small Ag nanoislands have a minor effect on the PL lifetimes

Model

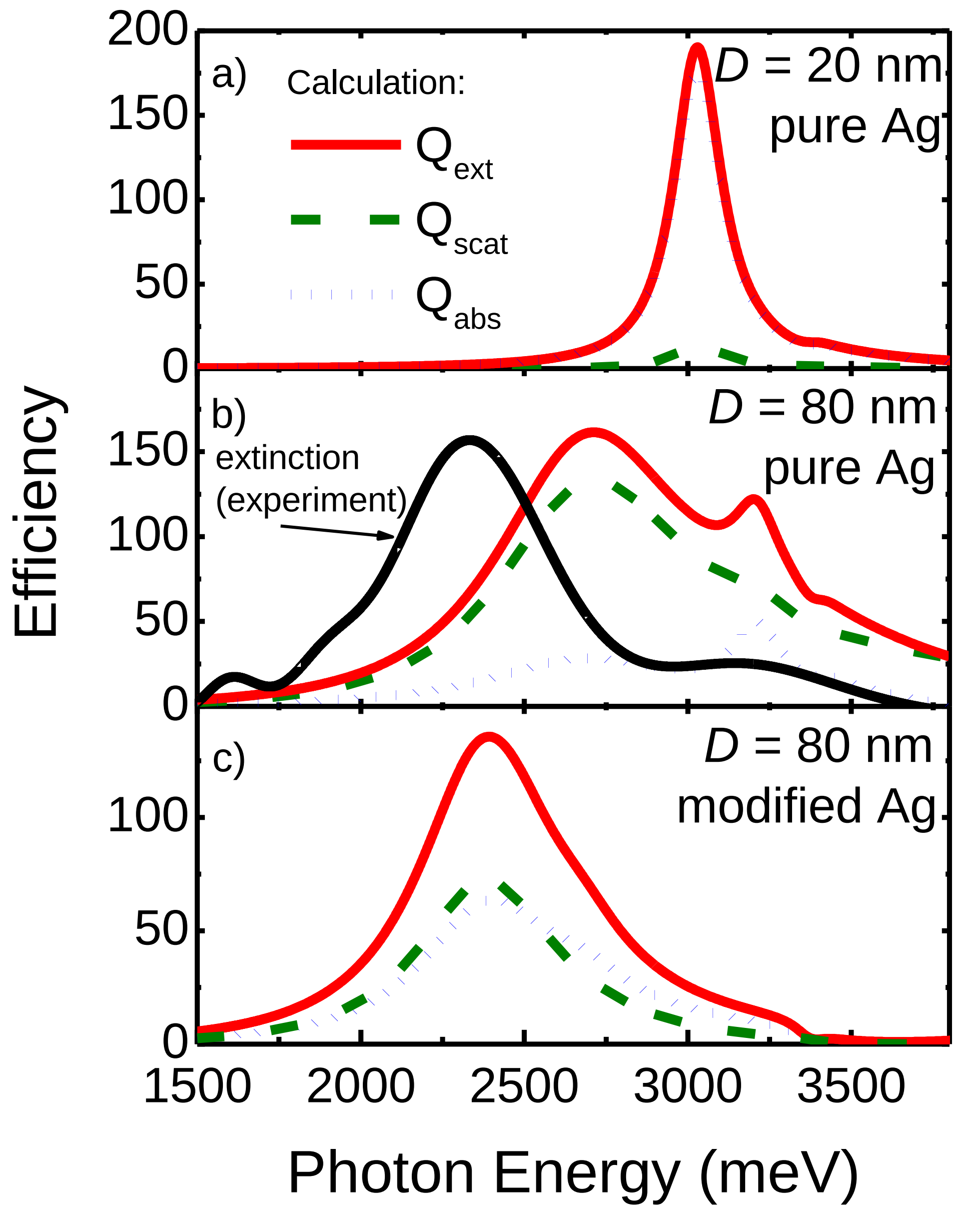
Mie scattering theory:
- the efficiencies Qscat, Qext, Qabs of scattering, extinction and absorption
- light interacting with a single spherical particle of a radius R
- the dielectric function of silver as in the classical Drude model

✓ Sample A: dielectric function of pure silver
$\varepsilon ib = 3.7$, $\gamma_{bulk} = 0.18$ eV, $\omega_p = 9.1$ eV

✓ Sample B: annealing at temperature of 750°C → interdiffusion of Ag and Zn → the effective parameters modified
$\varepsilon ib = 8.1$, $\gamma_{bulk} = 0.3$ eV, $\omega_p = 9.1$ eV

n_{ZnO} ⟶ following A. B. Djurišić et al., Appl. Phys. A, **43**, 37 (2003)

$$n_{out} = f n_{Air} + (1 - f) n_{ZnO}$$



- the extinction maximum shifts to lower energies when the radius of the sphere increases:

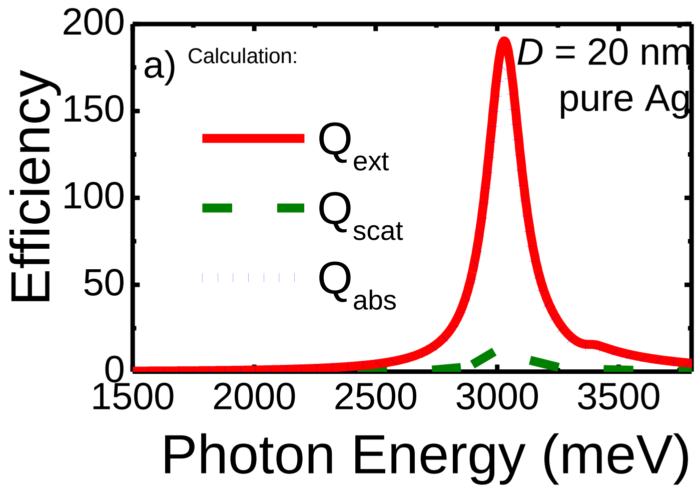
✓ sample A: D = 10-20 nm → energy of extinction maximum ~3 eV

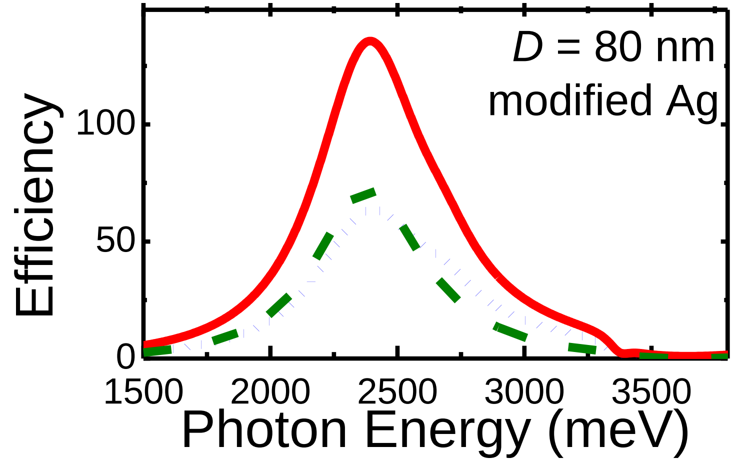
✓ sample B: D = 80-90 nm → energy of extinction maximum ~2.7 eV or ~2.4 eV

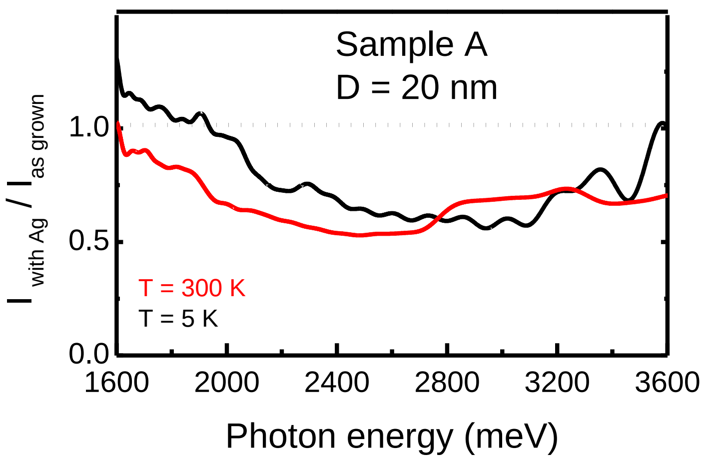
- increase of the sphere radius → a decrease of the absorption efficiency and an enhancement of the scattering efficiency

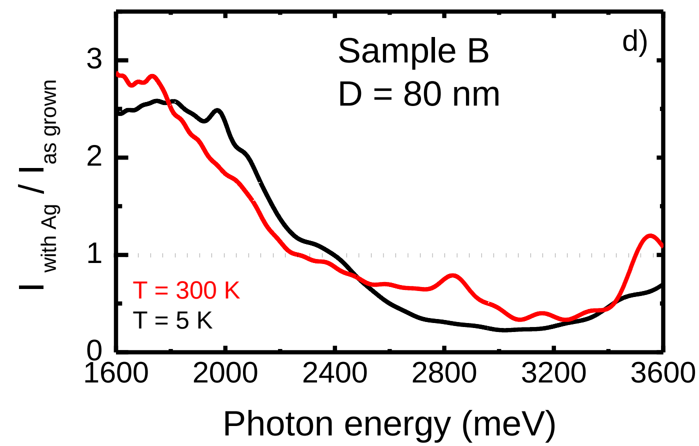
Model

Model









- Sample A : the absorption dominates over the scattering in the whole studied spectral range → a decrease of the PL intensity

- Sample B:
  - the absorption dominates over the scattering above 2.5 eV → a quenching of the emission
  - scattering dominates over the absorption → below ~2.5 eV emission enhancement

Conclusions

- The fabrication process, involving sputtering and annealing, has served to obtain Ag nanoislands of dimensions insuring the presence of the strong plasmonic effects.
- The temperature independent enhancement or quenching of the emission is observed and explained by the numerical model developed within the Mie theory.
- The ratio of the absorption to scattering efficiencies is found to govern the emission enhancement or quenching.
- The model highlights the impact of the sample preparation on the dielectric function of Ag.

Plan

- **QD CdTe/ZnTe** → MBE University of Warsaw → VIS

- **QW GaN/AlGaN** → MBE UNIPRESS and MOVPE University of J.Kepler Linz → UV:

- Porosity of the surface (UNIPRESS)

- Sputtering (islands) and lithographically defined metal nanostructures → Au, Ag, Al.

- variable distance from the surface to the emitter → optimal distance (strong plasmonic mode intensity and small intensity of noradiative process)