Optical Nonlinear Spectroscopy of Gold and Silicon Nanoparticles

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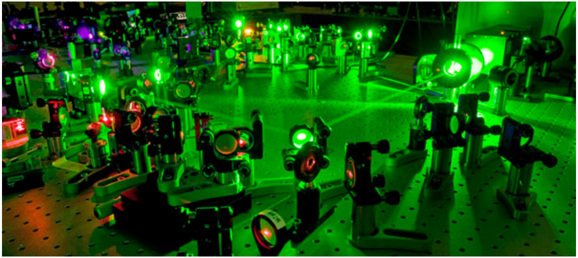
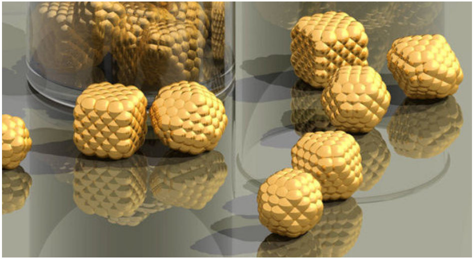
When you combine...

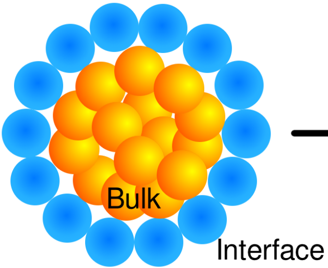


with these...



Historic use of metallic nanoparticles.[1]

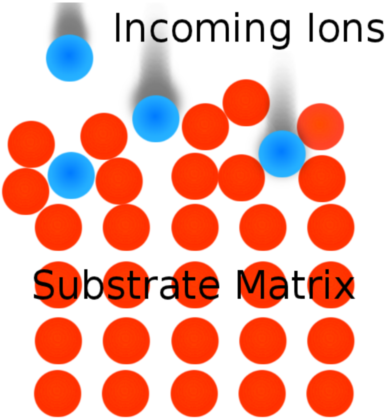
[1]Image: Raimond Spekking.



Nanoparticles have large surface to volume ratios.

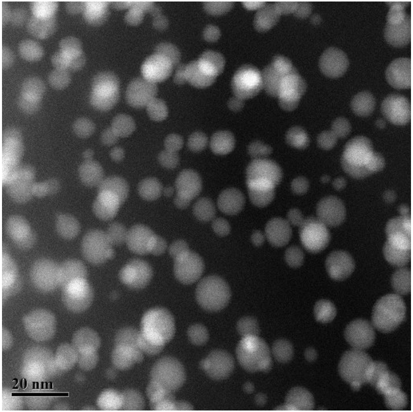
Our Samples[2]

- Created via ion implantation
- Implanted on Suprasil 300 substrate
- 8×8 and 8×4 mm transparent samples



[2] Provided by Dr. Alejandro Reyes and Dr. Alicia Oliver of the IF-UNAM.

Au Sample



TEM scan.

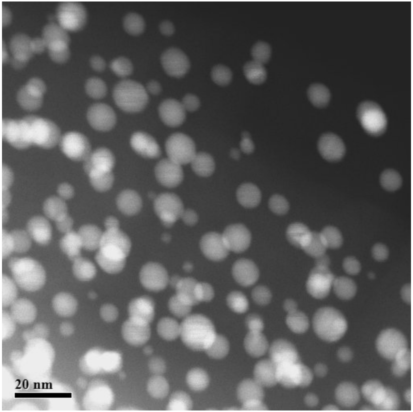
Specifications

- Size: ~ 3 nm
- Density: 5.8×10^{16} nps/cm^3
- Dose: 3.1×10^{16} atoms/cm^2
- Implantation Energy: 2 MeV

Au^{2+} Sample

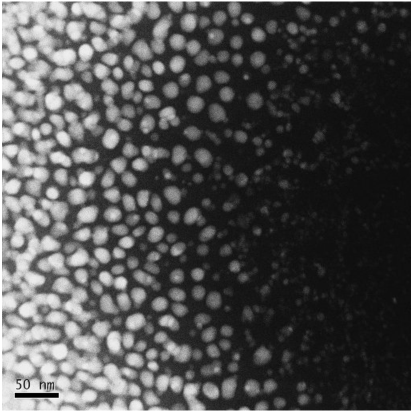
Specifications

- Size: ~ 3 nm
- Density: 9.8×10^{16} nps/cm^3
- Dose: 5.0×10^{16} atoms/cm^2
- Implantation Energy: 2 MeV



TEM scan.

Si Sample



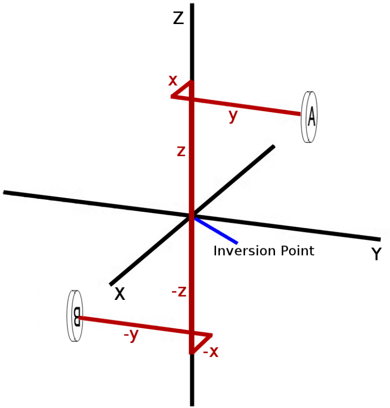
TEM scan.

Specifications

- Size: $\sim$ 20 nm
- Dose: 2.5×10^{17} atoms/cm^2
- Implantation Energy: 1.5 MeV

Centrosymmetric Materials

A centrosymmetric material is a material that displays inversion symmetry, such that $p(x, y, z) \rightarrow p(-x, -y, -z)$.

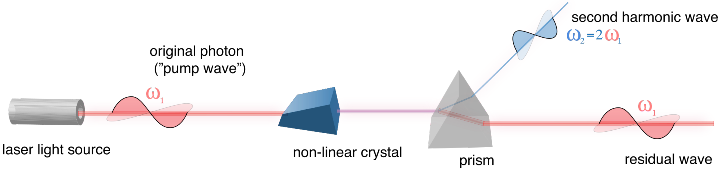


- Many nonlinear materials are centrosymmetric
- Nanospheres are definitely centrosymmetric
- The material in these nanoparticles is centrosymmetric

Second Harmonic Generation (SHG)

Characteristics[3]

- Two photons of the same frequency combine
- Create one photon of double the frequency

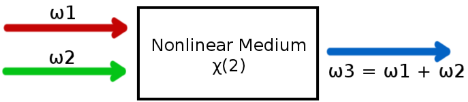


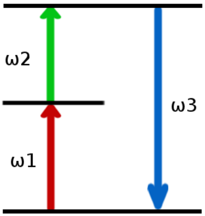
[3] Image: Jon Chui

Sum-frequency Generation (SFG)

Characteristics

- Two photons of different frequency combine
- Create one photon that is the sum of both frequencies





Second-order Nonlinear Effects

Early work[4] [5] demonstrated that second-order processes

- Are dipole forbidden in the bulk of centrosymmetric materials
- Are related to $\chi^{(2)}$, the nonlinear susceptibility
- Have bigger dipolar (surface) than quadrupolar contributions

Second-order processes are well studied for flat surfaces, but what about round materials like nanospheres?

[4] J.A. Armstrong et al. *Physical Review*, 127(6):1918–1939, Sep 1962.
[5] N. Bloembergen et al. *Physical Review*, 128(2):606–622, Oct 1962.

Nonlinear Response of Nanoparticles

- Early work[6] [7] show that nanospheres have both dipolar and quadrupolar contributions
- A few years later, Mochán et al.[8] determine the nonlinear polarization for an array of nanospheres.

[6] J.I. Dadap et al. *Physical Review Letters*, 83(20):4045–4048, 1999.
[7] V.L. Brudny et al. *Physical Review B*, 62(16):11152, 2000.
[8] W.L. Mochán et al. *Physical Review B*, 68(8):085318, 2003.

Theory

The dipole moment for a single nanosphere is

$$\mathbf{p}^{(2)} = \gamma^e \mathbf{E}^{\text{ex}}(0) \cdot \nabla \mathbf{E}^{\text{ex}}(0) + \gamma^m \mathbf{E}^{\text{ex}}(0) \times [\nabla \times \mathbf{E}^{\text{ex}}(0)] \,. \tag{1}$$

The quadrupole moment for a single nanoshpere is

$$\mathbf{Q}^{(2)} = \gamma^q \left(\mathbf{E}^{\text{ex}}(0)\mathbf{E}^{\text{ex}}(0) - \frac{1}{3}[\mathbf{E}^{\text{ex}}(0)]^2 \, \mathbf{1} \right), \tag{2}$$

where the γ's are unknown nonlinear response functions. $\mathbf{p}^{(2)}$ is nonlocal because of the field derivative, while $\mathbf{Q}^{(2)}$ is local.

The total nonlinear polarization for all the nanospheres is

$$\mathbf{P}^{nl} = n_s \mathbf{p}^{(2)} - \frac{1}{6} \nabla \cdot n_s \mathbf{Q}^{(2)}, \tag{3}$$

where n_s is the nanocrystal volume density. We substitute equations (1) and (2) to obtain

$$\mathbf{P}^{(2)} = \Delta' \left(\mathbf{E} \cdot \nabla \mathbf{E} \right), \tag{4}$$

where $\Delta' \equiv n_s \left(\gamma^e - \gamma^m - \gamma^q / 6 \right)$ and represents a kind of bulk response function.

Summary

Nonlinear response depends on

- Nonlocal excitation of the electric dipole moment
- Local excitation of the electric quadrupole moment
- The strength of the incident beam and
- The form (plane wave, Gaussian beam, polarization, etc.)
- The quadrupolar $(\mathbf{E} \cdot \nabla)\,\mathbf{E}$ term

What's the best way to enhance this signal?

The XP2SHG/SFG Technique

- Early work[9] shows that using two cross-polarized beams reduces the number of unknown $\chi^{(2)}$ components
- Wang et al. manage to discern surface and bulk contributions using two beams[10]
- Using two beams greatly increases the SHG/SFG signal usually enough to not need photon counters[11]

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[9] S. Cattaneo et al. *Optics Letters*, 28(16):144–1447, 2003.
[10] F.X. Wang et al. *Physical Review B*, 80(23):233402, 2009.
[11] P Figliozzi et al. *Physical Review Letters*, 94(4):47401, 2005.

Theory

The nonlinear polarization can be separated into two contributions[12],

$$\mathbf{P}_{nc}^{(2)} \equiv n_s \left(\gamma^e - \gamma^m - \frac{\gamma^q}{6}\right)(\mathbf{E}\cdot\nabla)\,\mathbf{E} \equiv |\Gamma_{nc}|e^{i\Phi}(\mathbf{E}\cdot\nabla)\,\mathbf{E}, \tag{5}$$

$$\mathbf{P}_{g}^{(2)} \equiv (\delta - \beta - 2\gamma)(\mathbf{E}\cdot\nabla)\,\mathbf{E} \equiv \Gamma_g(\mathbf{E}\cdot\nabla)\,\mathbf{E}. \tag{6}$$

The phase Φ causes interference between the glass and nanocrystal signals – this will cause the double peak shape we will see later on.

[12] A. Wirth et al. *Physica Status Solidi C*, 5(8):2662–2666, 2008.

Signal Enhancement

Single beam SHG scales as[13]

$$N_{SHG} \sim \frac{f_{\text{rep}}\mathcal{E}^2}{\tau A^2}, \tag{7}$$

where A is the beam spot size ($A = \pi w_0^2$), τ is the pulse duration, $\mathcal{E}$ is the pulse energy, and f_{rep} is the repetition rate of the pulses.

[13] P. Figliozzi et al. *Physical Review Letters*, 94(4):47401, 2005.

But for two incoming plane wave fields that are cross polarized, SHG counts scale as

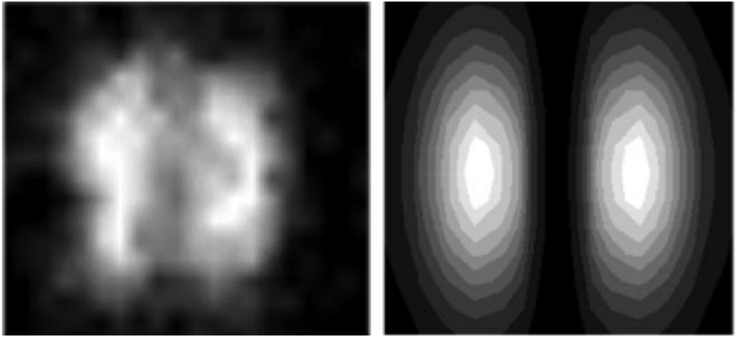
$$N_{SHG} \sim \frac{f_{\text{rep}} \mathcal{E}_1 \mathcal{E}_2 \sin^2 \alpha}{\lambda^2 \tau A^2}, \tag{8}$$

where α is the angle between the beams, and λ is the wavelength.

Enhancements

- The $\frac{1}{\lambda}^2$ factor greatly increases signal intensity
- The $\sin^2 \alpha$ term allows us to optimize the beam angle

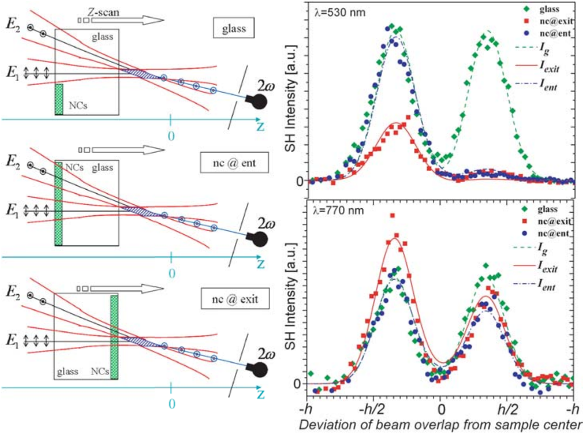
The $(\mathbf{E} \cdot \nabla)\,\mathbf{E}$ dependence is directly observable[14]:



Experiment (left) and predicted (right).

[14] P. Figliozzi et al. *Physical Review Letters*, 94(4):47401, 2005.

- Three Z-scans needed
- Interference between contributions causes double peak shape[15]



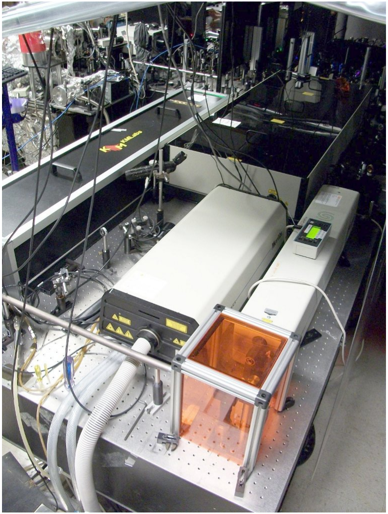
[15] A. Wirth et al. *Physica Status Solidi C*, 5(8):2662–2666, 2008.

Three huge benefits over single beam

1. Intensities are much higher
2. Enhanced signal allows better determination of $\chi^{(2)}$
3. Dipolar and quadrupolar contributions from nanoparticles can be discerned from substrate bulk contributions

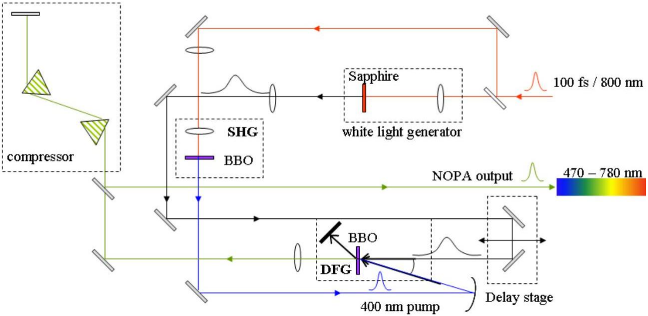
Laser system output

- Wavelength: 800 nm
- Average power: 1.1 Watts
- Energy: 1 mJ per pulse
- Duration: 100 fs
- Repitition rate: 1 kHz



Noncollinear Optical Parametric Amplifier

- 760 - 515 nm (1.6 - 2.4 eV)
- Energy: 3 - 12 μJ
- Duration: 250 fs
- Repitition rate: 1 kHz



The NOPA in action.

The XP2SHG/SFG Setup

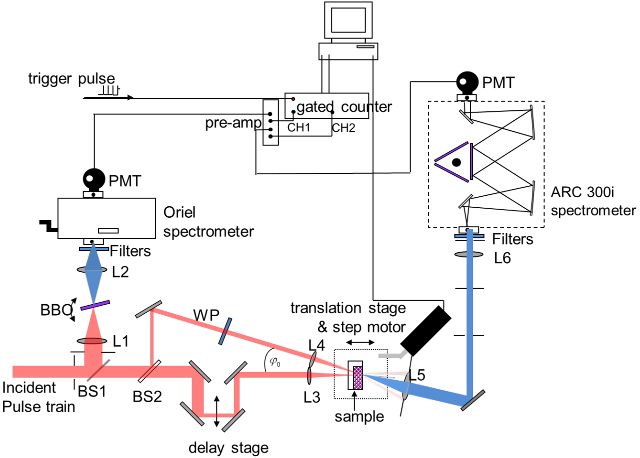
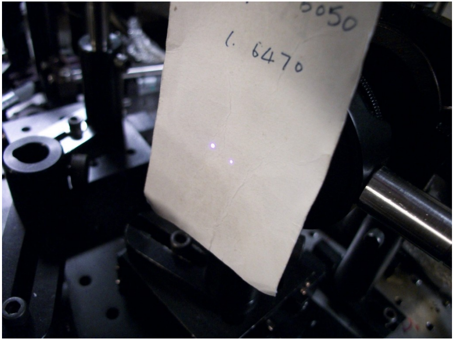
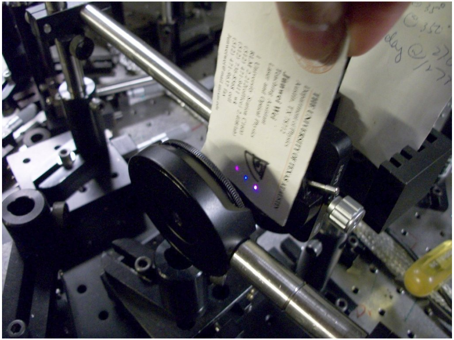


Diagram of the XP2SHG setup.

XP2SHG using a BBO crystal.

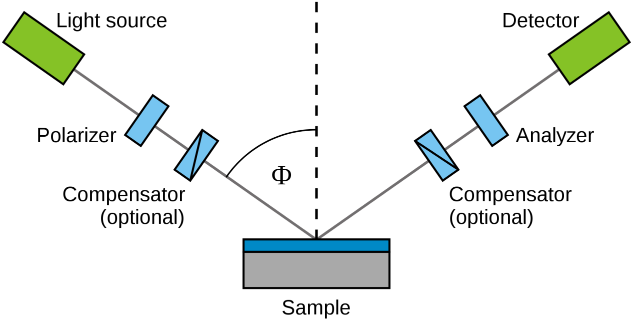


Two beams in. . .



three beams out!

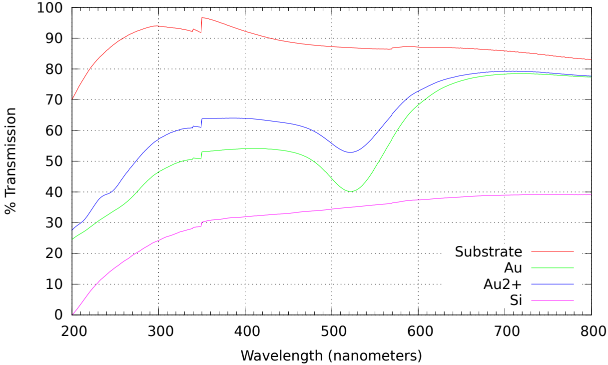
Ellipsometry[16]



- Complement nonlinear studies and allow full characterization of nanoparticles
- Ellipsometry can determine material dielectric function and complex index of refraction

[16] Image: Stannered

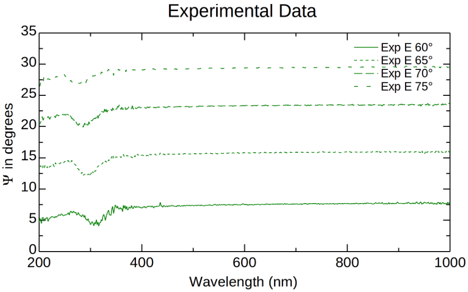
Linear Transmission

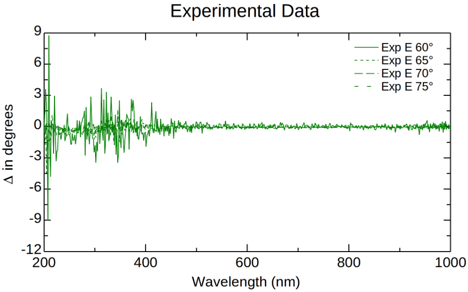


Gold samples have plasmon resonance around 530 nm[17] [18]

[17] D.M. Schaadt et al. *Applied Physics Letters*, 86:063106, 2005.
[18] S. Lin et al. *Advanced Materials*, 17(21):2553–2559, 2005.

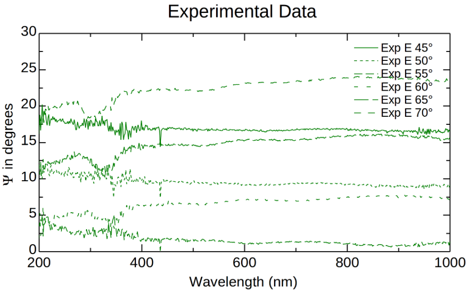
Ellipsometry – Substrate

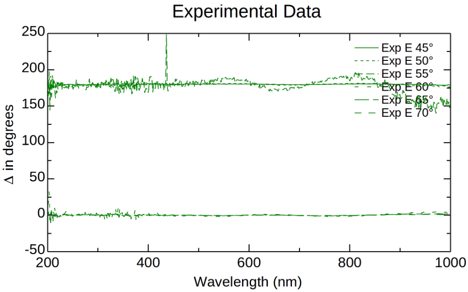




Graphs for Ψ (left) and Δ (right).

Ellipsometry – Gold

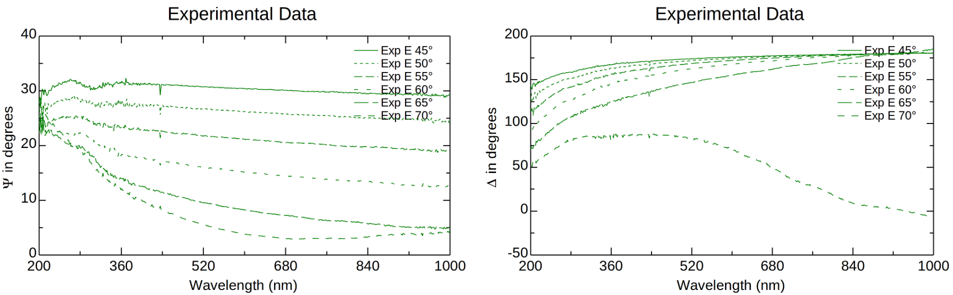




Graphs for Ψ (left) and Δ (right). Very noisy, nothing like references[19]

[19] H.L. Zhang et al. *Advanced Materials*, 15(6):531–534, 2003.

Ellipsometry – Silicon

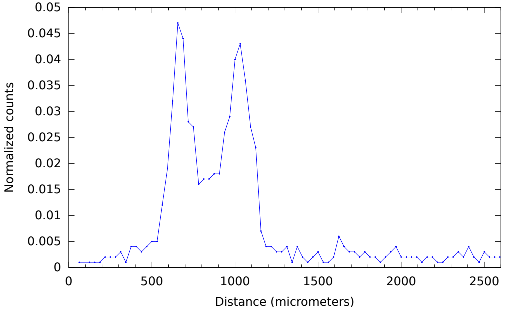


Graphs for Ψ (left) and Δ (right). Flat transmission curve for Silicon and poor ellipsometry data nothing like previous work.[20]

[20] J. Wei et al. *Physical Review B*, 84:165316, Oct 2011.

XP2SHG/SFG – Substrate

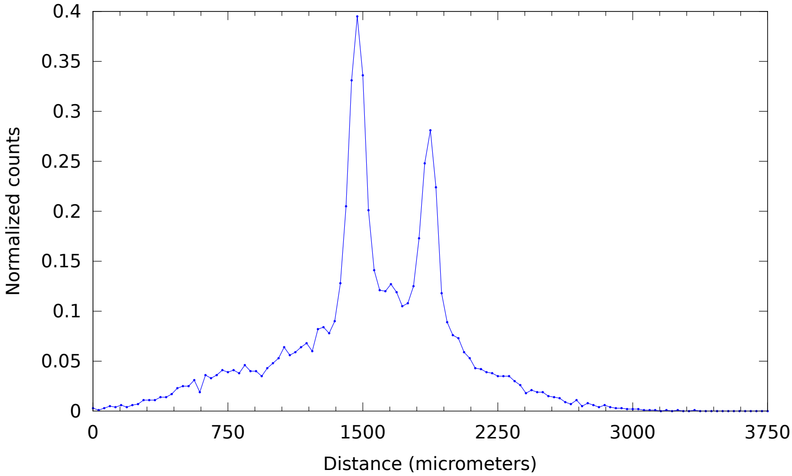
Substrate XP2SFG data at 550 + 800 nm.



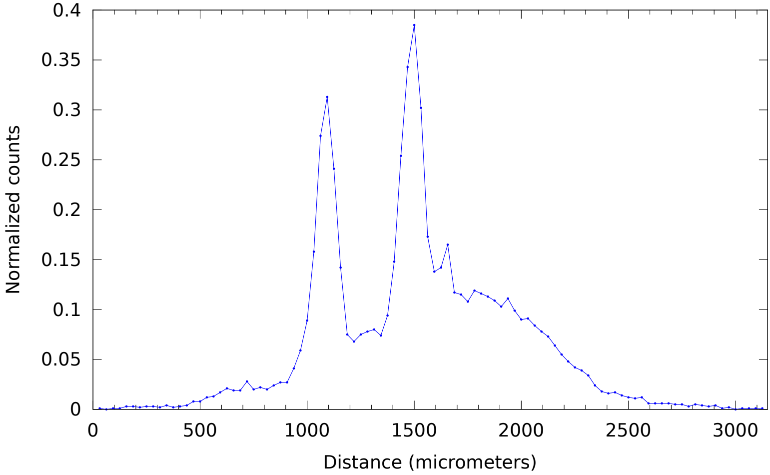
Confirms results from previous studies[21] [22]

[21] J. Wei et al. *Physical Review B*, 84:165316, Oct 2011.
[22] A. Wirth et al. *Physica Status Solidi C*, 5(8):2662–2666, 2008.

XP2SHG – Gold



Gold XP2SHG data, entry side.

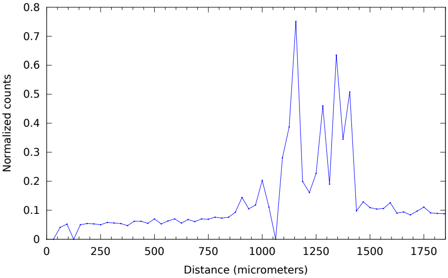


Gold XP2SHG data, exit side.

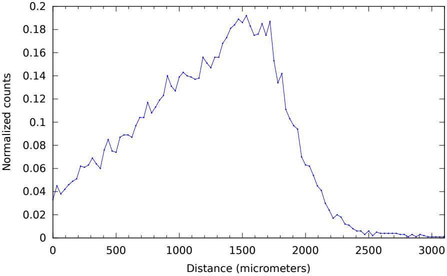
Characteristics

- Almost identical to substrate data!
- Low input intensity produces no SHG/SFG output
- High input intensity generates white light
- Need to analyze entry and exit positions
- Detector can't distinguish between single and two-beam SHG
- Both dipolar and quadrupolar contribution

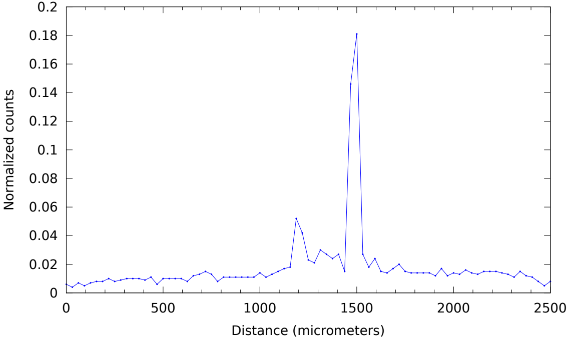
XP2SFG – Gold



Noisy signal with no discernible peaks at 520 + 800 nm



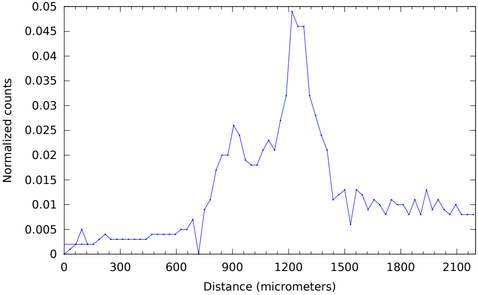
White light generation at 560 + 800 nm



Best XP2SFG data at 520 + 800 nm.

- Three different frequencies: NOPA in, 800 nm in, SFG out
- Strong output with NOPA frequency near plasmon resonance
- Wider angle between beams should alleviate scattering

XP2SHG/SFG – Silicon



XP2SFG at 500 + 800 nm.

- Weaker signal compared to Au
- Signal not enhanced at all[a] [b] [c]

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[a] J. Wei et al. *Phys. Rev. B*, 84, 2011.
[b] A. Wirth et al. *Phys. Stat. Sol. C*, 5(8), 2008.
[c] P. Figliozzi et al. *Phys. Rev. Lett.*, 94, 2005.

Summary

- Samples of poor optical quality with massive scattering
- Scattering and transparency to blame for erratic linear data
- XP2SHG/SFG technique did not enhance nonlinear signal
- Exciting near resonance may have actually been a hinderance
- Separate Z-scans did not allow for separation of glass and nanoparticle contributions

"So what?"

Conclusions

Accomplished

- Applied the XP2SHG/SFG technique
- Applied complementary linear measurements
- Gained considerable experience

Future Work

1. Samples need to be in better shape and better characterized
2. Samples mounted on different substrates for linear measurements
3. XP2SHG/SFG technique still relatively new with metallic nanoparticles
4. Implement this setup here at the CIO

Acknowledgements

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¡Gracias!

¡Feliz cumpleaños a Alberto, Marcelo
&
Edith
y feliz aniversario también!