Effect of nanoscale surface roughness on surface-tuned nanoparticle plasmon resonances

Chatdanai Lumdee and Pieter G. Kik

CREOL, the College of Optics and Photonics, UCF, Orlando, FL, USA

Outline

- Introduction: substrate-coupled metal nanoparticles
  - Attractiveness
  - Resent studies

- All inorganic substrate-coupled gold nanoparticles
  - Resonance control using Al₂O₃ coatings
  - Stability under laser irradiation

- Effect of surface roughness on gold nanoparticle resonances
  - Observations
  - Experiment
  - Model and simulation

- Summary
Introduction

Substrate-coupled nanoparticles: attractiveness
- High field enhancement in the gap

CST Microwave Studio®

At 633 nm

60 nm diameter Au NP on Al₂O₃ coated Au film

Introduction

Substrate-coupled nanoparticles: attractiveness
- High field enhancement in the gap
- Easy to control coupling strength
Introduction

Substrate-coupled nanoparticles: attractiveness
- High field enhancement in the gap
- Easy to control coupling strength
- Robust, reproducible, simple, and inexpensive

60 nm diameter Au NPs on 3.4 nm Al₂O₃ coated gold film
substrate-coupled nanoparticles
- Effective polarizability of a point dipole near a metal surface

- A sphere couple to a metal substrate

- Absorption by a small sphere above a substrate
Recent studies

substrate-coupled metal nanoparticles (examples)

- Distance-dependent plasmon resonant coupling between a gold nanoparticle and gold film

- Substrates matter: Influence of an adjacent dielectric on an individual plasmonic nanoparticle
Recent studies

substrate-coupled metal nanoparticles (examples)
- **Sensors**
  Plasmonic smart dust for probing local chemical reactions

Tailoring surface plasmons of high-density gold nanostar assemblies on metal films for surface enhanced Raman spectroscopy
J. Lee, et al. Nanoscale 2014, 6 (p.616)

- **Plasmonic ruler**
  Plasmon ruler with angstrom length resolution
  M. W. Knight, et al. ACS Nano 2012, 6 (p.9237)
Recent studies

substrate-coupled nanoparticles (examples)
- *Plasmonic absorber*

Controlled-reflectance surfaces with film-coupled colloidal nanoantennas

Near-infrared broadband absorber with film-coupled multilayer nanorods

- *Nonlinear optics*

Plasmon gap mode-assisted third-harmonic generation from metal film-coupled nanowires
Recent studies

substrate-coupled nanoparticles (examples)
- Photoluminescence enhancement

Gap-plasmon enhanced gold nanoparticle photoluminescence
C. Lumdee, et al. (submitted)
Recent studies

substrate-coupled nanoparticles (examples)
- *Photoluminescence enhancement*

Gap-plasmon enhanced gold nanoparticle photoluminescence
C. Lumdee, et al. (submitted)
Recent studies

substrate-coupled nanoparticles (examples)
- Photoluminescence enhancement
Gap-plasmon enhanced gold nanoparticle photoluminescence
C. Lumdee, et al. (submitted)

> 4 orders of magnitude enhancement

Very fun!
Want to know more? Meet after the talk
Outline

- Substrate-coupled metal nanoparticles
  - Attractiveness (*simple, robust, reproducible*)
  - Recent studies

- All-inorganic substrate-coupled gold nanoparticles
  - Resonance control using $\text{Al}_2\text{O}_3$ coatings
  - Stability under laser irradiation

- Effect of surface roughness on gold nanoparticle resonances
  - Observations
  - Experiment
  - Model and simulation

- Summary
Outline

- Substrate-coupled metal nanoparticles
  - Attractiveness (simple, robust, reproducible)
  - Recent studies – applications need resonance control

- All-inorganic substrate-coupled gold nanoparticles
  - Resonance control using Al$_2$O$_3$ coatings
  - Stability under laser irradiation

- Effect of surface roughness on gold nanoparticle resonances
  - Observations
  - Experiment
  - Model and simulation

- Summary
All-inorganic substrate-coupled gold nanoparticles

Why?
Previous attempts
→ Organic molecule spacer layer
→ Organic background
→ Possibly not very stable

Our structure
Gold nanoparticles on aluminum and gold film
→ Stable Al₂O₃ coating on the surface

All-inorganic substrate-coupled gold nanoparticles

Gold nanoparticles on aluminum film
→ Anodizing aluminum to control Al₂O₃ thickness
→ NP-to-NP resonance tuning range from 580 – 550 nm

Microscopy images

Before Anodization

3 V

6 V

9 V

Scattering spectra (from one NP)

All-inorganic substrate-coupled gold nanoparticles

Gold nanoparticles on aluminum film

→ Improve tuning range limited by 3.6 nm native Al₂O₃
→ Tuning range from 690 – 610 nm for 0 – 3.4 nm Al₂O₃
All-inorganic substrate-coupled gold nanoparticles

Gold nanoparticles on Al₂O₃ coated substrates

→ Wide tuning range of 140 nm (690-550 nm = far red to green)


Gold nanoparticles on Al$_2$O$_3$ coated substrates stability

Stable structure $\rightarrow$ good for applications e.g. sensing and photoluminescence

Outline

- Substrate-coupled metal nanoparticles
  - Attractiveness *(simple, robust, reproducible)*
  - Recent studies – applications need resonance control

- All inorganic substrate-coupled gold nanoparticles
  - Resonance control using Al$_2$O$_3$ coatings
  - Stability under laser irradiation

- Effect of surface roughness on gold nanoparticle resonances
  - Observations
  - Experiment
  - Model and simulation

- Summary
Effect of surface roughness on gold nanoparticle resonances

Why?
Previous works
→ Resonance tuning of Au NPs on all inorganic substrates
→ Spectral variations

Q1: What causes this?
A1: Particles, size and shape.
Q2: What about surface of substrate?

This study
Gold nanoparticles on a gold film
→ Mapping local surface roughness
→ Simulate particle’s scattering spectra
→ Compared predicted and measured spectral variations

Effect of surface roughness on gold nanoparticle resonances

How?

Dark-field microscopy and spectroscopy

50x objective

Gold film

Glass substrate

Au NP
Effect of surface roughness on gold nanoparticle resonances

Results

Single gold nanoparticle scattering spectra

What causes this?
Size variation cannot make this!
How we model surface roughness???

80 nm diameter Au NPs on Au film

Effect of surface roughness on gold nanoparticle resonances

How? – Modeling surface roughness

Challenges
1) Accessing local surface near each nanoparticle
2) Randomness of surface morphology and particle locations
3) Infinite number of possible scenarios → infinite simulations?
...

Effect of surface roughness on gold nanoparticle resonances

How? – Modeling surface roughness

Finding local height seen by a nanoparticle
Effect of surface roughness on gold nanoparticle resonances

How? – Modeling surface roughness

What to defined in simulation?
Roughness period, roughness radius of curvature and height
Effect of surface roughness on gold nanoparticle resonances

How? – Modeling surface roughness

What to defined in simulation?
Roughness period, roughness radius of curvature and height

Effect of surface roughness on gold nanoparticle resonances

How? – Modeling surface roughness

Roughness period (P) = 25 nm,
Roughness radius of curvature (R_p) ~ 32 nm

What to defined in simulation?
Roughness period, roughness radius of curvature and height
Effect of surface roughness on gold nanoparticle resonances

How? – Modeling surface roughness

Roughness period \( (P) = 25 \text{ nm} \),
Roughness radius of curvature \( (R_p) \sim 32 \text{ nm} \)
Effect of surface roughness on gold nanoparticle resonances

How? – Modeling surface roughness

Roughness period \( P = 25 \text{ nm} \),
Roughness radius of curvature \( R_p \approx 32 \text{ nm} \)
Roughness height is determined by the gap size \( d \)
Effect of surface roughness on gold nanoparticle resonances

How? – Modeling surface roughness

Roughness period (P) = 25 nm,
Roughness radius of curvature (R_p) \sim 32 \text{ nm}
Roughness height is determined by the gap size (d)
Effect of surface roughness on gold nanoparticle resonances

How? – Numerical simulation

\[ P_{\text{rad}} \propto |\mu_z|^2 \omega^4 \]


CST Microwave Studio® and Au dielectric function from literature

Effect of surface roughness on gold nanoparticle resonances

Results

Simulated gold nanoparticle scattering spectra

Variation due to surface roughness (gap variation)
Effect of surface roughness on gold nanoparticle resonances

Results

Simulated gold nanoparticle scattering spectra

Variation due to surface roughness (gap variation)
Effect of surface roughness on gold nanoparticle resonances

Results

Simulated gold nanoparticle scattering spectra

Variation due to surface roughness (gap variation)
Effect of surface roughness on gold nanoparticle resonances

Results

Simulated and measured gold nanoparticle scattering spectra

Variation due to surface roughness (gap variation)
Effect of surface roughness on gold nanoparticle resonances

Summary
Surface roughness can contribute to spectral variation.

The effect is difficult to estimate due to infinite possible scenarios.

Use an AFM image to predict nanoparticle locations and model local surface.

Statistically calculate scattering spectra and spectral variation of gold nanoparticles on a thermally evaporated gold film.

The calculation seems to be in a good agreement with the measured data.
1) Introduction and current studies on substrate-coupled metal nanoparticles

2) All-inorganic substrate-couple resonances $\rightarrow$ broad tuning range and stable structure

3) Significant part of spectral variation comes from surface roughness. This spectral variation can be predicted using an AFM image and numerical simulations.