Angular tuning of plasmonic inter-particle coupling probed by spectroscopic ellipsometry

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Abstract

Localized surface plasmon resonances in metallic nanoparticles are known to be really sensitive to the polarization state of the incident electromagnetic wave which excites them. In this paper, we investigate the polarization dependence of localized surface plasmon resonances in gold nanorings on top of a continuous gold layer and a dielectric spacer. By scanning the incident angle in spectroscopic ellipsometry measurements, we tune the inter-particle coupling of the localized plasmon resonances, as the apparent particle density seems to be modified for the incident wave. Sharp phase transitions are observed around the dipolar plasmon resonance of the coupled nanoring/dielectric/metal film nanostructure, for both polarization states of the incident wave. We anticipate that these phase transitions can be applied for extremely sensitive refractive index sensing with an improved tunability and higher figures of merit.

1. Introduction

Spectroscopic ellipsometry is a powerful tool for the characterization of the optical properties and thickness of dielectric and optically thin metallic layers. By measuring both the phase and amplitude of a reflected light beam with a modulated polarization (between P or TM and S or TE polarized) for a certain angle of incidence, it allows to derive the optical properties of the sample under investigation. In this paper, we show that it is also a very powerful tool to study localized plasmon resonances in randomly distributed gold nanorings on top of a continuous gold film and a dielectric spacer. These samples were fabricated by colloidal lithography [1,2].

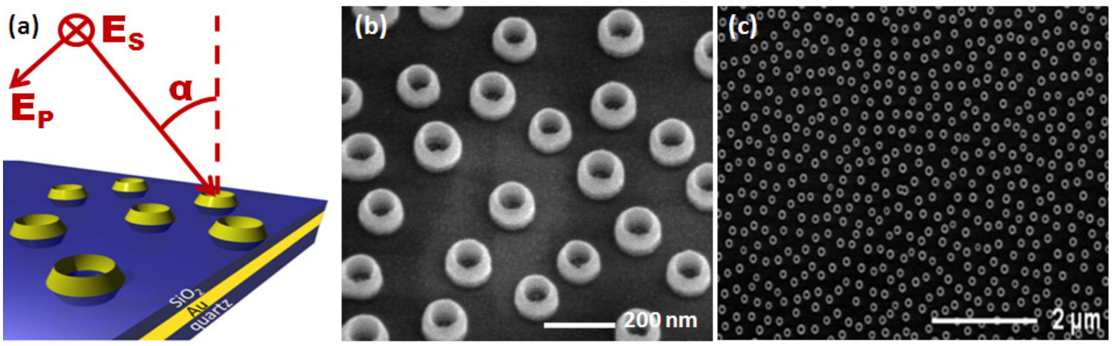

Fig. 1: Investigated nanoparticles: (a) Schematic representation of the measurement configuration, (b) Detailed SEM picture of Au nanorings, (c) Large-area SEM picture showing the uniform random particle distribution.

The localized surface plasmon resonances in nanoparticles exhibit strong dependence on the polarization of the incident wave. By scanning the angle of incidence, the relative interparticle coupling is altered, giving rise to a pronounced narrowing and spectral shifting of the plasmon resonance with increasing angle of incidence. At the same time, the degree of P- or S-like character of the incident wave is enlarged or reduced, which results in large differences for the reflected signals. Here we study the near-infrared electric dipole resonance of gold nanorings, which can be excited in with both polarizations. When the plasmon mode is excited with an S-polarized wave, we directly excite the electric dipole mode of the ring, which capacitively couples to image charges in the underlying

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gold layer, giving rise to an electric quadrupole mode and a magnetic dipole mode in the oxide. For a P-polarized wave on the other hand, the electric quadrupole mode is excited directly by polarizing the gap between the ring and the gold layer, which is accompanied of a magnetic dipole in the oxide (see fig. 2). Obviously, the interparticle coupling strongly depends on the incident polarization, as it determines the nature of the plasmon resonance and the coupling mechanism with respect to neighbouring particles. The inter-particle coupling can be mediated by electric field coupling (dipole-dipole and quadrupole-quadrupole interaction) or by magnetic field coupling (dipole-dipole interaction). Depending on the dominant coupling mechanism, the plasmon resonance shows a blue shift if the scattered fields of the neighbouring particles enhance the local resonance or a red shift in case the scattered fields weaken the local resonance. In case of our gold nanorings which have an average interparticle distance of only 250nm, the P-resonance shows a blue-shift with increasing angle of incidence, due to magnetic dipole coupling, while the S-resonance shows a red-shift with increasing angle of incidence due to electric dipole/quadrupole coupling.

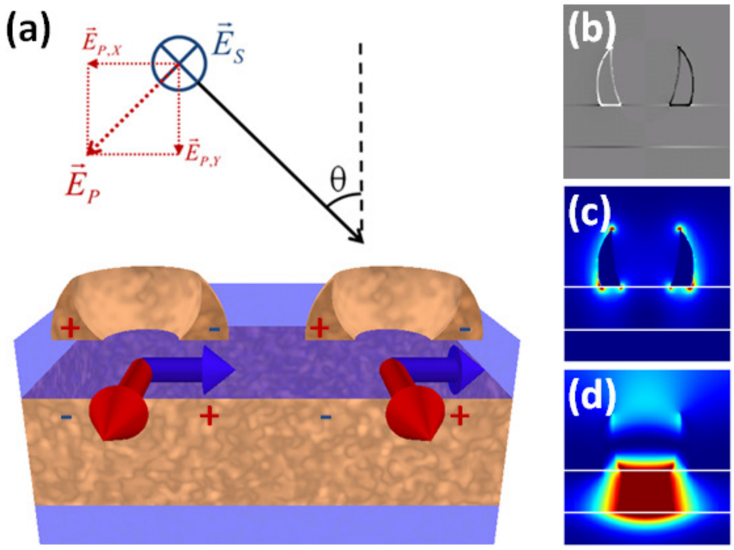

Fig. 2: Overview of the involved plasmonic modes. (a) Schematic overview of the quadrupole mode for P-polarization and the induced magnetic dipoles for P (red arrow) and S (blue arrow). (b) Charge density plot at resonance. (c) Electric field distribution at resonance. (d) Magnetic field distribution at resonance.

Our spectroscopic ellipsometry measurements were carried out on a commercial GESP5 [3] ellipsometer. The polarization is modulated by a rotating polarizer at the incident side while lock-in measurements of the reflected beam provide us with the phase information of the plasmon resonances. The relation between the measured quantities is described by the main equation (1) of ellipsometry:

$$\rho = \frac{r_p}{r_s} = \tan(\Psi).e^{i\Delta} = \tan(\Psi).[\cos(\Delta) + i\sin(\Delta)] \quad (1)$$

The reflection ratio between P- and S polarized beams is given by the value of *tan(Ψ)*, while the phase difference (Δ) between the reflected signals is given by the value of *cos(Δ)*

2. Results and discussion

An overview of the angle-dependent ellipsometry measurements is given in figure 3 (panels a and b). For all investigated angles we observe the P-polarized resonance at shorter wavelengths than the S-polarized resonance (fig 3.a). For both resonances, sharp phase jumps are observed between the reflected signals with P- and S-polarization in the value of *cos(Δ)* (fig 3.b). These phase transitions occur when the free electrons in the gold particles make the transition between in- and out-of-phase oscillations with respect to the incident wave. This phenomenon is observed at the central frequency of the localized surface plasmon resonances, where phase jumps up to 180˚ occur.

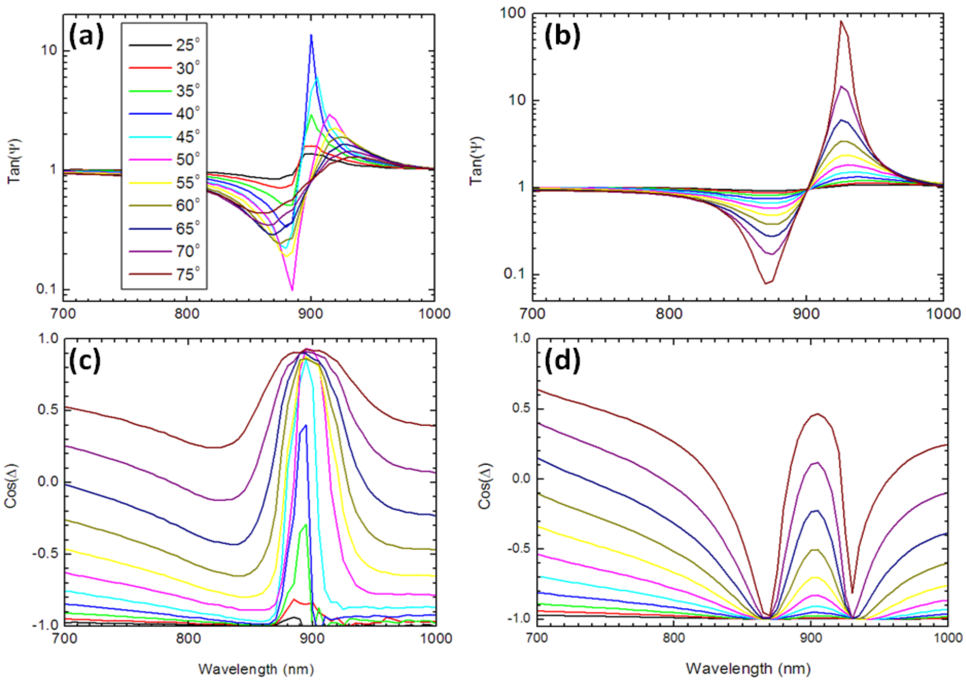

Fig. 3: Measured (a and c) and simulated (b and d) values of tan(Ψ) and cos(Δ) for the coupled nanoring/oxide/gold layer system.

In the measurements we clearly observe that the P-resonance blue shifts and the S-resonance red shifts with increasing angle of incidence. On top of that, we observe narrowing of the line widths of the plasmon resonance, resulting in an increase of the maximum and a decrease of the minimum values for *tan(Ψ)* with increasing angle of incidence. At an incidence angle of 55˚ we observe an amplitude maximum in this ratio, which gradually decreases again for larger angles. This decrease can be attributed to a decrease in the apparent particle density at large angles, which results in an increase of the overall reflected power and a less pronounced plasmon resonance. The most narrow phase jumps are observed for incidence angles close to 55˚, where the values of *cos(Δ)* reflect a phase transition of almost 180˚.

We clearly observe very similar features in the FEM simulation data [4], which were extracted for a periodic array of disks with a pitch that matches the average inter-particle spacing of our samples. The main differences between the measured and simulated data can be attributed to the random particle distribution of our samples, which gives rise to inhomogeneous broadening and hence a slight modification of the inter-particle coupling.

4. Conclusion

We have shown that spectroscopic ellipsometry is a powerful tool for studying localized plasmon resonances and their phase-behaviour. By scanning the angle of incidence and polarization state of the incident wave, intrinsically broad dipole resonances can be probed with really narrow line widths, opening up possibilities for extremely sensitive refractive index sensing.

References

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