Propagating surface plasmons on nanoporous gold

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Abstract

Nanoporous gold films are prepared using a dealloying method and form a sponge type bi-continuous network. As the structure sizes are below 50 nm the material forms an effective medium with a negative dielectric constant for near infrared light. The dispersion relation of the propagating surface plasmons on the air/nanoporous gold interface is determined from reflection measurements in the Kretschmann configuration. A characteristic red-shift by ca. 0.85 eV compared to surface plasmons on solid gold layers is observed. The results are compared with calculated dispersion relations applying the Bruggeman effective medium theory for the nanoporous gold films.

1. Introduction

Surface plasmons at metal/dielectric interfaces have wavelengths shorter than light and exhibit a strong field confinement at the interface. Because of these properties they form the backbone of current sub-wavelength optics. Their dispersion relation on a plane interface between two semi-infinite metallic and dielectric media follows directly from Maxwell's equations [1] and is given as:

$$k_x = \frac{\omega}{c}\sqrt{\frac{\varepsilon_m \cdot \varepsilon_d}{\varepsilon_m + \varepsilon_d}} \qquad (1)$$

where, k_x describes the wave vector of the surface plasmon and ε_m and ε_d are the dielectric constants of the metal and the dielectric respectively.

To control the dispersion of the surface plasmons, usually ε_d is varied. However, here in our experiments we explore the possibility to tune the dispersion of surface plasmons by changing the value of ε_m by introducing a nanoporosity into the metal. In this way a "meta-metal" is created whose effective dielectric constant ε_m is less negative than the bulk metal dielectric constant. This is expected to have a direct consequence for the surface plasmon dispersion on the nanoporous metal surface.

2. Sample fabrication and structural investigation

We prepared nanoporous gold films by dealloying white gold leaves, which consist of a 50 wt.% - 50 wt.% mixture of gold and silver, in HNO_3. The ca. 100 nm thick leaf is floated on 65% HNO_3 for 10 min, 30 min and 60 min, rinsed afterwards and finally placed on a glass slide. During the floating on HNO_3 the Ag is dissolved from the film. The more noble gold atoms remain and aggregate due to surface diffusion [2] resulting in a disordered nanoporous gold film of sponge-type appearance (Fig.1).

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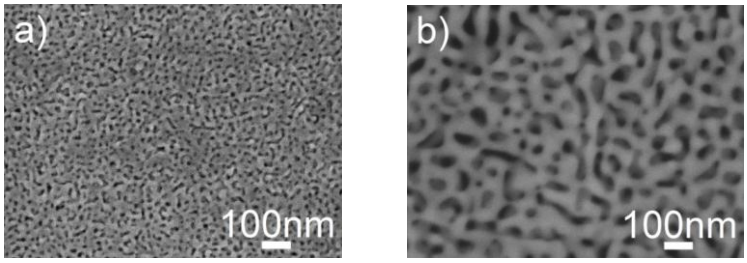

Fig. 1. SEM images of samples dealloyed in 65% conc. HNO_3 for different times a) 10 min, b) 60 min. After dealloying the film consists of an irregular bi-continuous network of air pores and gold veins forming a nanoporous gold film.

As the leaching time increases, the average pore size diameter varies from 12 nm to 30 nm. After 60 mins of dealloying, all the silver of the original white gold leaf is dissolved in the acid and the film consists of pure gold. Only this 60 min dealloyed film is considered further and its optical properties are compared with a ca. 50 nm thick, pure, non-porous "bulk" gold film, which was deposited on a glass slide by thermal evaporation.

3. Optical porperties

Ellipsometric measurements were performed and the complex effective dielectric constants of the bulk and nanoporous gold films was determined.

To excite the propagating surface plasmons on the air/metal interface we employ the prism coupling technique (Kretschmann configuration). Our setup allowed the measurement of angular resolved reflection spectra with incidence angles in the range of $45°<\theta<68°$. For p-polarized light a characteristic dip in reflectivity is observed, which shifts to shorter wavelengths with increasing angle of incidence (Fig 2). The shift of the dip in p-polarized reflectivity is characteristic for the excitation of a propagating surface plasmons at the metal/air interface.

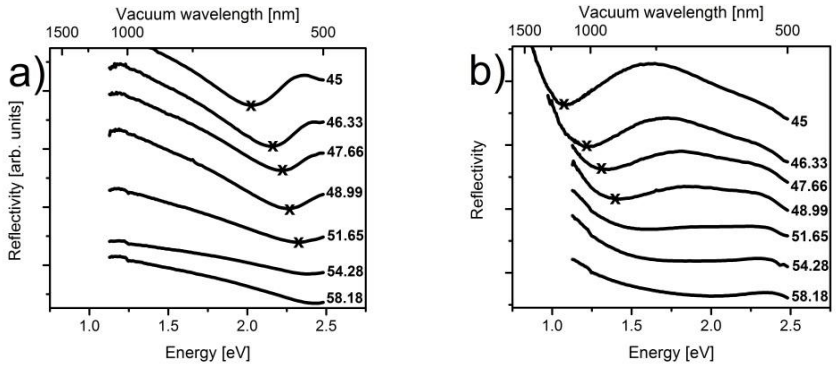

Fig. 2. p-polarised angular resolved reflectivity spectra measured in Kretschmann configuration. The value of the angle of incidence θ in the glass is indicated on each curve. a) bulk gold film, b) nanoporous gold film. The dip in reflection shifts to shorter wavelengths with increasing angle of incidence (indicated by the crosses). This indicates the resonant excitation of propagating surface plasmons.

Considering the frequency ω and the angle of incidence of the reflection dip the in plane wave vector k_x is determined for which the SPs are excited. From the obtained data points (k_x,ω) for the excitation of the SPs the dispersion relation of the SPs is mapped (Fig 3).

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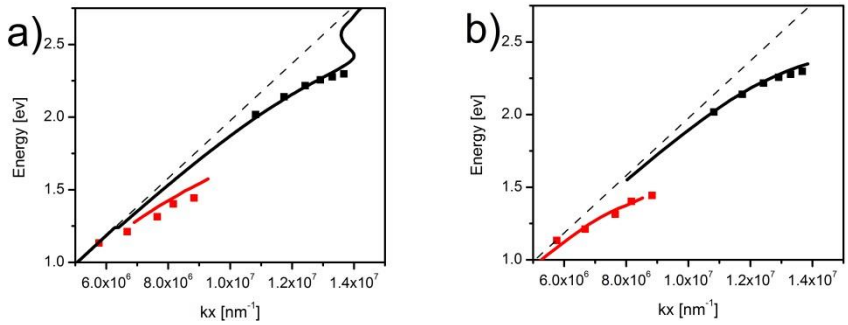

Fig. 3. Dispersion relation of propagating surface plasmons at the bulk gold film (black) and the nanoporous gold film (red). Experimentally determined data are shown as squares, while dispersion curves determined from theoretical calculations are shown as lines. a) Theoretical calculations are based on ellipsometrically determined dielectric constants b) Theoretical calculations are based on effective dielectric constants determined by the Bruggeman formula

Comparing the dispersion curves of the bulk gold/air SP and the nanoporous gold/air SP a clear red shift by approximately 0.85 eV of the SP dispersion relation for the nanoporous gold is observed. This confirms that the SPs can be spectrally shifted to the near infrared region by introducing a nanoscopic porosity in the metal film. The increase of ε_{eff} due to the porosity (i.e. less negative ε_{eff}) causes a red shift of the surface plasmons at the same wave vector k_x or a corresponding increase of k_x at fixed surface plasmon frequency ω.

The experimentally determined dispersion curves are compared with theoretical calculations in two ways. First we used the experimentally determined dielectric constants from the ellipsometric measurements for both films, calculated the reflection spectra for the multilayer-system glass/film/air and mapped the dispersion relation from the calculated resonance dips as described above. In a second approach the Bruggemann effective medium theory is applied to determine the effective dielectric constant of the nanoporous gold layer. From the SEM-images of the film an air filling factor of f=0.5 is estimated. The comparison of the experimentally determined dispersion curve with these theoretical calculations shows a remarkable agreement especially for the Bruggemann-based calculation.

The relatively wide dips in reflectivity indicate larger losses in the nanoporous gold which are probably caused by increased scattering from the rough surface and smaller Au grain sizes. These losses could be reduced in recently prepared nanoporous gold layer, which were fabricated by evaporation of Au on self ordered nanoporous alumina membranes. In these new samples the reduced surface scattering lead to sharper reflection dips for the excitation of the surface plasmons.

5. Conclusion

In conclusion the experiments and analysis proves that the dispersion relation of the SPs can be controlled by the porosity of the metal film. Introducing a nanoporosity with structural sizes well below the wavelength of light creates a "meta-metal" with an effective dielectric constant leading to a distinct red shift of its SP dispersion relation. Moreover it was demonstrated, that the SP dispersion on the nanoporous gold film can be predicted rather well in the near IR applying the Bruggemann theory for the disordered bi-continuous network of gold veins and air pores. These results bridge the gap between the classic surface plasmons on plane bulk metal layers with frequencies in the visible and the designer plasmons at corrugated metal surfaces in the microwave and Terahertz domain.

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