Modeling of plasmon resonance of silver nanoparticles on a silicon surface

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Abstract. Silver nanoparticles have unique optical properties due to resonance effects that arise due to the presence of conduction electrons in them. When these electrons interact with photons, they can create localization of electric fields at the interfaces with the environment. Silver nanoparticles deposited on a transparent substrate are often used for research, while Ag nanostructures on Si are studied in this work. They have great potential for practical applications. The interaction of light with nanostructures can be described using various models (pseudo-dielectric functions, effective medium, thin-layer structures, etc.) and optical methods for the experimental determination of their parameters (refractometry, spectrophotometry). Bulk plasmon resonance is considered in this work, which is excited when plasmons are excited at their resonant frequency by an external electromagnetic wave. Calculations were performed for different diameters of silver nanoparticles on a silicon substrate with different structure periods. The calculated spectra are in good agreement with the experimental data of the obtained samples. As a result of the plasmon resonance modeling, the position of the plasmon resonance depends on the density of the arrangement of silver nanoparticles, with an increase in the displacement resonance towards the long-wavelength region.

1. Introduction
Silver nanoparticles have unique optical properties due to resonance effects that arise due to the presence of conduction electrons in them. When these electrons interact with photons, they can create localization of electric fields at the interfaces with the environment [1]. The use of plasmon resonance is possible in various fields: nanoelectronics [2], optoelectronics [3], biomedicine [4] and to develop energy conversion devices [5]. The main quality of this effect is its sensitivity to the environment [6], which can be used as a rather sensitive detector. However, to apply this effect, it is necessary to accurately predict the properties of plasmon resonance: position, width, and amplitude. In [7], spherical nanoparticles are well described analytically by using the Mie equation, but it is also worth noting that the environment has a strong effect on plasmon resonance. Placing a particle on a substrate causes difficulties in calculating its properties. The substrate has influences on the particle when the particles are formed by the deposition method. Their shape changes to more like a hemisphere and this has an impact on the plasmon characteristics. All these factors complicate the modeling and calculation of this system. Investigation and control of these changes will make it possible to obtain a rather simple technological method of manufacturing by chemical deposition and an easier
implementation of them as a sensor, since an electronic logic device can be formed on the same silicon wafer.

2. **Experiment**

A layer of silver nanoparticles was obtained by chemical deposition from a 0.02 M AgNO3 + 5M HF solution in a ratio of 1: 4 (N1) and 1: 8 (N2), respectively, on a p-type c-Si substrate with a resistance of 13 Ohm·cm after which was annealed at 350 °C in air. The obtained samples have an average size of 100 nm and filling factor 40% (N1), 34% (N2), which was calculated using SEM images in the MATLAB software package (Figure 1).

![Figure 1. SEM image of silver nanoparticles after annealing at 350 °C (a) N1, (b) N2](image)

The reflection spectra for p- and s-polarization (Figure 2) were obtained at an incidence angle of 70° by an SE-2000 spectral ellipsometer (Semilab).

![Figure 2. Reflection spectra at p- (a) and s-polarization (b) of silver nanoparticles after annealing at 350 °C for samples N1, N2 and silicon substrate (Calculated from the optical constant c-Si [8])](image)

3. **Modelling of Ag nanoparticles on Si**

A model for analyzing the optical properties of silver nanoparticles was built, a schematic view is shown in Figure 3 (a).

The silver particle has a spheroid shape. It is located on a silicon substrate and the model is an array of particles, shown in Figure 3 (b).
Figure 3. Schematic representation of the model in the Comsol Multiphysics: cross section (a) and view from above (b)

After specifying the geometric parameters of the model, the boundary conditions were set:
- port 1 is located on the upper face of the model (parallel to the substrate). It is parallel to the substrate and emits a plane wave. Polarization s (has an electric field vector E, perpendicular to the plane of incidence) or p (has an electric field vector E, parallel to the plane of incidence) is set in port 1;
- periodicity conditions are set on the side faces;
- the lower body of the model is a perfectly matched layer. This physical element of the model does not reflect, but only absorbs radiation. This condition makes it possible not to break the entire thickness of the substrate into finite elements, which allows to reduce the size of the model. Parasitic radiation has a strong influence on the result, if the substrate is thin. It reflected from the lower boundary of the model.

The calculations were done for the cell and particle size. The geometry parameters of the model were based on the SEM images of the samples (Figure 1) and several close values of it for the best comparison of the calculated spectra with the measured ones. The finite element method is used in computation, which means breaking the model into the small tetrahedron and calculating the electric field strength vector for each of them according to Maxwell’s equations. The optical constants of silver and silicon are taken from [8].

Figure 4 (a) shows the calculated spectra of the constructed model in the Comsol Multiphysics program for a particle diameter of 100 nm with their period from 130 nm to 170 nm with a step of 10 nm. It is a dip in Rp specter around 320 nm which is an influence of volume plasmon resonance [9].

Figure 4. Calculated spectra Rp of a layer of silver nanoparticles at an angle of incidence of 70° for a silver nanoparticle with a period from 130 to 170 nm (a); and comparison of the measured spectra Rp obtained from samples N1 and N2 and calculated (b).
As a result of calculations (Figure 4 (a)), it was found that the plasmon resonance at a wavelength of about 320 nm has a slight shift to longer wavelengths with a decrease in the volume fraction of silver, with a constant particle diameter of 100 nm. This effect is the influence of decreasing number of Ag nanoparticles and rising impact of Si substrate in reflection. The best convergence with N1 and N2 is occurred to models with the period of 160 nm and the particle diameter of 100 nm (Figure 4 (b), Calc1), the period of 165 nm and the particle diameter of 110 nm (Figure 4 (b), Calc2).

4. Conclusion
Structures of silver nanoparticles on the silicon surface were obtained in this work. They looked like disordered spherical particles, which were obtained from an island film with irregularly shaped nanoparticles. The model was designed in the program Comsol Multiphysics. Then calculating spectra were compared with experimental ones. Since the experimentally obtained structure is a disordered matrix of silver nanoparticles with a spread in sizes and distances, complete coincidence of the calculated and experimental spectra could not be achieved, because the calculation was based on a hexagonal lattice of hemispheres with a given diameter and period. The tendency of short-wavelength shift of the position of the volume plasmon resonance at 320 nm was detected with an increase in the volume fraction of silver in the structure.

Due to the performed calculations, by setting the sizes of silver nanoparticles and the distance between them in the array, it is possible to predict the behavior of resonances.

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