Synthesis and studying properties of the GNPs@Fe$_x$O$_y$ structure

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Abstract. An article presents a study of the regularities of the formation of gold up to 8 nm thick, deposited by vacuum thermal deposition on silicon wafers with a natural oxide, its annealing and subsequent deposition of iron oxide by chemical vapor deposition. The stages were accompanied by SEM analysis of the sample surface, as well as fixation of the optical and FTIR spectra, I–V characteristics of the obtained structures.

1. Introduction
Iron oxide is a widespread compound, interest in which is justified by the presence of various phases with significantly different properties. It is obtained in the form of particles and films by chemical vapor deposition, plasma-chemical methods, magnetron sputtering, etc [1]. The selected method allows to obtain a phase with desired properties. At the same time, the subsequent modification of such a material can lead to a significant change in certain properties. Therefore, the study of laws of formation and basic properties (optical and electrical) is quite urgent.

In turn, the patterns of gold formation are of great interest in connection with the manifestation of LSPR, and the combination of surface plasmon resonance and oxide matrices is relevant for a variety of sensors - gas sensors, IR reflectors, SERS etc [2,3].

In work, gold of various thicknesses was deposited on n-Si silicon substrates by vacuum thermal sputtering. Then, by chemical deposition from the gas phase, iron oxide (Fe$_2$O$_3$) was applied (the process is described in more detail here [4] at a temperature of 250 °C. At the same time, gold was annealed with different thicknesses. The thickness of the gold was determined by the RBS method. Gold-oxide coatings were studied by scanning electron spectroscopy, spectrophotometry, IR spectroscopy. An I–V characteristics were also measured using two probe method.

2. Methodology
In this work, gold of various thicknesses was deposited on silicon substrates n-Si by vacuum thermal spraying. Then, iron oxide was applied by chemical vapor deposition at a temperature of 250 °C. At the same time, gold of various thicknesses was annealed. The thickness of gold was determined by the RBS method (Rutherford backscattering spectroscopy).
Gold-oxide coatings were studied by scanning electron spectroscopy Zeiss Supra, spectrophotometry (Shimadzu UV-3600 Plus spectrophotometer), IR-spectroscopy (FSM 1201), Reflection high-energy electron diffraction (RHEED). The study was made of electrical properties using I–V measurements.

3. Results

3.1 Surface morphology

The thickness of the coatings was measured by Rutherford backscattering spectroscopy. The gold thicknesses were 1, 1.5, 2.5, 3, and 6 nm. Results are presented in Figure 1. Then the resulting structures were annealed in an argon atmosphere at a reduced pressure \( P = 1000 \text{ Pa} \) and temperature of 250 °C. In one case, they were only annealed, in the other case, they were annealed and iron oxide was applied (the technology is described in more detail in [5]).

![Figure 1. Measurements of gold film thickness by Rutherford backscattering spectroscopy.](image)

Figure 2a-e shows SEM images of the surface of samples coated with gold of various thicknesses. The study of the formation patterns showed that on the natural oxide, gold of a smaller thickness (less 2 nm) forms particles, and with an increase in the thickness of the structure known as "golden islands".

After gold deposition SEM images of the deposited films were recorded (Figure 2 f-j). This series of images is characterized by a sequential increase in the specific surface area occupied by gold, while spherical particles are characteristic for thicknesses less than 2 nm and with an increase in thickness structures called golden islands were formed.

![Figure 2. SEM-images during different steps of formation.](image)

At the second step, during the annealing of such structures, the surface morphology of the sample changes; at the same time, at thicknesses less than 2 nm, the particles agglomerate and at large thicknesses, after annealing, the specific area occupied by gold decreases.
At the last step, gold is coated with iron oxide at a temperature 250 °C. A uniform coating of gold particles with iron oxide occurs while maintaining the shape of the original surface (Figure 2 k-o, while the crystallinity of iron oxide increases with an increase in the initial thickness of gold).

With the simultaneous folding of gold and the application of iron oxide on thin films, particles of two types were formed, the structures of the "golden islands" type were simply covered, while maintaining the topology as in simple annealing. The type of crystals is most characteristic of alpha-iron oxide (as it was proven by RHEED) and have a trend for formation crystals with gold thicknesses increasing.

### 3.2 Optical measurements

The optical reflection spectra are presented for gold and gold with iron oxide in the range of 200-1600 nm. It can be seen that for both groups of spectra, the maximum reflection is in the region of 800 nm, while for samples without iron oxide, a maximum is observed in the region of 300 nm, which is typical for silicon. 6 nm gold with iron oxide also has a minimum reflection (7%) in the region of 500 nm.

IR-spectra show a decrease in the transmission intensity of gold, while the 6 nm film almost completely absorbs IR-radiation. Films of smaller thickness have peaks characteristic of silicon and its oxide and a lower transmission intensity. Figure 3 shows the optical reflectance spectra of the obtained structures (gold and gold with iron oxide).

![Figure 3](image)

**Figure 3** Optic spectra of: a) Si/SiO$_2$ with gold nanoparticles annealed at 250 °C; b) Si/SiO$_2$/GNPs@Fe$_x$O$_y$, c) view of FTIR spectra of Si/SiO$_2$/GNPs@Fe$_x$O$_y$ structures.

The nature of the spectra for 1 and 1.5 nm is very similar. In this case, the spectra 1, 1.5, 2.5 nm of gold-iron oxide reflection are characterized by the form of the spectrum, characterized by a maximum reflection at 860, 300 and 400 nm. While the structures GNP s @ Fe$_x$O$_y$ 3 and 6 nm gold thickness have a gentler bend in the 200-400 nm region, and in the 400-600 region the sample has a pronounced minimum of reflection.

Figure 3c shows a view of the IR spectra of GNP s-Fe$_x$O$_y$ samples. The IR-spectra were recorded in transmission mode. IR-spectroscopy of gold films is not very common because gold films are good reflectors of IR-radiation. Nevertheless, it can be seen that with decreasing film thickness, the reflection intensity decreases, and at 2.5 and 3.0 nm gold thicknesses have a shoulder typical for silica and thick film when 6 nm nearly absolutely reflect gold.

### 3.3 I-V measurements

The I–V characteristics of the samples were obtained using a two-probe measurement method. Measurements were made using a Keithley 2400 current source and voltage meter. The I–V measurements of the samples were obtained at a longitudinal displacement. Two gold contacts were deposited on the surface of the structure. A halogen lamp was used as a light source. All
measurements were carried out under the same illumination conditions. Figure 4 shows the I-V characteristics of the samples at longitudinal displacement.

From the graphs presented in Figure 4 it can be seen that the nature of the dependences in the absence and presence of irradiation for the samples is different. As the thickness of the initial gold film increases, the value of the photoinduced current decreases and the behavior of the I–V characteristic changes. The ohmic character of the dependence begins to dominate from the barrier character as the film thickness increases, which is associated with an increase in the degree of filling the substrate surface with the deposited materials. To understand the behavior of the I – V characteristics of the samples consider Figure 5.

![Figure 4. I-V measurements of structures with and without illumination. The inset picture shows zoomed image of I-V measurements.](image)

Based on Figure 5, it can be assumed that the photo-response of the obtained samples changes depending on the initial thickness of the gold film. As the thickness of the initial gold film increased, an extreme value of the photoinduced current was observed. With increases of the film thickness the ohmic nature of the dependence begins to prevail on the barrier character. Presumably, this is due to the thickness of the final coating after the deposition of iron oxide the efficiency of light capture and separation of charge carriers.

![Figure 5. Dependence of ratio of light and dark currents from initial gold thickness.](image)

4. Conclusions
We presented a study of the regularities of the formation of gold up to 8 nm thick, deposited by vacuum thermal deposition on silicon wafers with a natural oxide, its annealing and subsequent deposition of iron oxide by chemical vapor deposition. The stages were accompanied by SEM analysis of the sample surface, as well as fixation of the optical and FTIR spectra, I–V characteristics of the obtained structures.
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