Synthesis of core-shell Ag/SiO\(_2\) nanoparticles for SPASER structures

D V Viazmitinov, L B Matyushkin, A I Maximov
St Petersburg Electrotechnical University “LETI”, 197376 St Petersburg, Russia
E-mail: dviazmitinov@gmail.com

Abstract. Aqueous solution of colloidal silver was prepared using a method based on a chemical reaction of silver nitrate water-soluble salts and sodium borohydride. Synthesized silver nanoparticles were analyzed by transmission optical spectroscopy. Silica shells were formed by the modified Stöber process. During shell formation nanoparticles were also doped by organic dye (Rhodamine 6G). The resulting structures were deposited on silicon substrates. Half of the samples were annealed at 300°C, and the other half was just dried. Processed samples were investigated by atomic force microscopy.

1. Introduction
Nowadays nanoplasmonics is one of the most rapidly growing areas of physics and nanotechnology. It has many possible applications ranging from sensing and biomedicine to imaging and information technology. One of the most significant problems in this field of science is development of devices that can generate coherent plasmonic fields – SPASER’s (Surface Plasmon Amplification by Stimulated Emission of Radiation) [1]. There are two main types of such devices – planar structures, consist of metal nanostructure separated from a two-level energy system by a dielectric layer [1] and core-shell structures in which the dielectric layer surrounds the metallic core, separating it from the two-level system [2]. Core-shell structures can be synthesized by methods of colloid chemistry, which allows to produce them cheaper and more massively than planar structures requiring quite expensive and inefficient process technologies. Different methods and materials are used to produce core-shell structures for nanoplasmonics. The most suitable material for the core are considered noble metals such as gold [2] or silver [3]. Stable and monodisperse silver nanoparticles can be simple synthesized by method, described below. Technology of producing shells with predetermined thickness and composition still needs to be elaborated.

2. Experimental
Aqueous solution of colloidal silver was prepared using a method based on a chemical reaction of water-soluble salts of silver nitrate and sodium borohydride:

\[ \text{AgNO}_3 + \text{NaBH}_4 \rightarrow \text{Ag} + \frac{1}{2} \text{H}_2 + \frac{1}{2} \text{B}_2\text{H}_6 + \text{NaNO}_3 \]

A volume fraction of 10\(^{-3}\) M aqueous silver nitrate solution was slowly added dropwise to three volumetric fractions cooled in an ice bath 2 \(\times 10^{-3}\) M aqueous solution of sodium borohydride. Use of an excess of sodium borohydride is because it acts both as reducing and stabilizing agent. As a supplement to sodium borohydride, polyvinylpyrrolidone was added for greater stabilization of the particles size. The resulting silver colloidal solution is due to a plasmon resonance absorption spectrum with a peak near 400 nm \(\lambda_{pl}\) has a transparent yellow color. Full width at half maximum (FWHM) is 50-70 nm. The peak position essentially depends on particle size (Table 1).
Table 1. Relation between particle diameter and form of the optical spectrum

| Particle diameter $d$, nm | $\lambda_{pl}$, nm | FWHM, nm |
|---------------------------|-------------------|-----------|
| 10-14                     | 395-405           | 50-70     |
| 35-50                     | 420               | 100-110   |
| 60-80                     | 438               | 140-150   |

Dynamics of particle stability is shown at fig.1.

![Graph showing absorbance over wavelength](image)

**Fig. 1. Ag nanoparticles stability dynamics**

Transmission optical spectroscopy showed that the particle size in the result solution of colloidal silver is 12 nm.

Silica shells were formed by the modified Stöber process:

1. Silver nanoparticle sol was diluted with isopropyl alcohol in a volume ratio of 1/200 in an ultrasonic bath.
2. The resulting solution was stirred in an ultrasonic bath at 40°C for 1 hour.
3. Then, aqueous ammonia solution was added into the solution.
4. After temperature stabilization, tetraethoxysilane (TEOS) was injected in an amount that depends on the total surface of the silver particles and the desired thickness of the shell (it was assumed that all TEOS transformed into silica).

The final ratio of the reactants is shown in table 2.

Table 2. The final ratio of the reactants

| Reactant         | Value, ml |
|------------------|-----------|
| NH$_3$OH         | 10,50     |
| Distilled water  | 18,00     |
| TEOS             | 0,13      |
| Isopropyl alcohol| 50,00     |
During shell formation nanoparticles were also doped by organic dye (Rhodamine 6G). It was made by adding aqueous solution of rhodamine 6G (10 ml, 25%) before injection of TEOS in the above-described silica shells formation technology. The resulting structures were cleared by sedimentation process and then investigated using optical transmission spectroscopy (fig. 2) and photoluminescence test (fig. 3).
The resulting structures were deposited on silicon substrates. Half of the samples were annealed at 300°C for 15 minutes, and the other half was just dried for 1 hour. Then all of the samples were analyzed using the atomic force microscopy in tapping mode (fig. 4).

Fig. 4. Atomic force microscopy images for dried (left) and annealed (right) samples

3. Results
Atomic force microscopy showed that the synthesized core-shell structures have a size approximately equal to 150 nm and variation in size is approximately 5 nm. The images obtained allow us to conclude that the calculation of the thickness of the silica shell is quite exactly the same as the actual thickness of the shells of the synthesized nanoparticles. By comparing the two groups of samples (dried and annealed), it can be concluded that annealing increases the uniformity of particle distribution over the substrate, and also reduces the variation in size. Analysis of the absorption and fluorescence spectra indicates that the resulting nanoparticles are able to absorb a wide wavelength range, while having a relatively narrow photoluminescence peak. Considering that source for photoluminescence excitation radiation is a laser with a wavelength of 455 nm, and the photoluminescence peak falls on 540 nm, we can assume that the rhodamine molecules are excited by the energy generated by silver nanoparticles.

References
[1] David J Bergman and Mark I Stockman 2003 Physical Review Letters 90(2) 027402-1.
[2] M A Noginov, G Zhu, A M Belgrave, R Bakker, V M Shalaev, E E Narimanov, S Stout, E Herz, T Suteewong & U Wiesner 2009 Nature 460(27) 1110.
[3] V V Hardikar, E Matijevic 2000 Journal of Colloid and Interface Science 221 133.
[4] A I Maximov, V A Moshnikov et al, Fundamentals of sol-gel technology of nanocomposites, St Petersburg: Technomedia, Elmor, 2007.