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# Saturable absorber based on silver nanoparticles for passively mode-locked lasers

D.A. Glubokov, V.V. Sychev, A.S. Mikhailov, A.E. Korolkov,
D.A. Chubich, B.I. Shapiro, A.G. Vitukhnovskii

*Abstract.* **A saturable absorber based on plane (tabular) stabilised silver nanocrystals, which is promising for picoseconds laser systems operating in the range 650–900 nm, is studied. This material has a plasmon decay time of about 2 ps, while its absorption at a pump intensity of 10 MW cm$^{-2}$ decreases by 1.6%, which is sufficient for using this crystal for passive mode locking.**

***Keywords:*** *saturable absorber, passive mode locking, silver nanoparticles, pump–probe method, nonlinear absorption.*

In recent years, passively mode-locked lasers attract increasing interest and find application in optical communications, medicine, material treatment, and fundamental investigations [1]. These lasers are advantageously distinguished from actively mode-locked lasers by compactness, relatively simple design, and lower cost. The key element of passively mode-locked lasers is a saturable absorber. Its material must have the following optical properties: a high absorption coefficient at low optical radiation intensities, a low absorption coefficient at high intensities, and a short relaxation time of the bleached state. These properties are inherent in, for example, semiconductor saturable absorber mirrors (SESAMs) [2]. However, their application in laser systems is less convenient and more expensive than the use of proposed by us saturable absorbers based on silver nanoparticles. Plasmonic saturable absorbers can be made in the form of organic films with nanoparticles of a given shape and size distributed in the volume of a photographic gelatine matrix, as well as can be created by direct laser photolithography. Taking into account the promising methods of forming silver nanoparticles on the edges of optical fibres by STED nanolithography (direct two-beam laser lithography with the use of luminescent photostimulators), the study of these materials for application in fibre laser systems is a topical problem [3, 4].

**D.A. Glubokov, A.E. Korolkov, D.A. Chubich** Moscow Institute of Physics and Technology (State University), Institutskii per. 9, 141700 Dolgaprudnyi, Moscow region, Russia; P.N. Lebedev Physics Institute, Russian Academy of Sciences, Leninsky prosp. 53, 119991 Moscow, Russia; e-mail: daglubokov@gmail.com, wm.nn.gp@gmail.com, chubich@sci.lebedev.ru;
**V.V. Sychev, A.G. Vitukhnovskii** P.N. Lebedev Physics Institute, Russian Academy of Sciences, Leninsky prosp. 53, 119991 Moscow, Russia; e- mail: vladivas@list.ru, alexei@sci.lebedev.ru;
**A.S. Mikhailov, B.I. Shapiro** M.V. Lomonosov Moscow State University of Fine Chemical Technologies, prosp. Vernadskogo 86, 119571 Moscow, Russia; e-mail: m5483@yandex.ru, bishapiro@mail.ru

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We study a saturable absorber based on silver nanoparticles embedded into a photographic gelatine matrix. This material has a high laser radiation resistance and is optically transparent and extremely chemically stable, which is important for passivation of polygonal silver nanoparticles and allows one to efficiently use it in laser engineering.

In this work, we used multistage synthesis, which consists in successive introduction of silver nitrate and reducing agents – hydroquinone and $Na_2SO_3$ – into alkaline aqueous solution of gelatine at a high temperature. The synthesis was performed using chemically pure $AgNO_3$ and alkaline solution of photographic gelatine. The aqueous solutions of silver sols were prepared using doubly distilled water. The suspension was synthesised in a thermostatted stainless steel reaction vessel 500 mL in volume. The reaction mixture was stirred by a mechanic stirrer with a controlled number of rotations. The total synthesis time was 26 min. After synthesis, the suspension was placed into a refrigerator to form a gel, which was then milled and multiply washed with cooled distilled water. After washing, the suspension was melt at 43–45 °C, added with 1 mL of 50% phenol solution, and stored in a refrigerator. To prepare coloured gelatine layers, the suspension was 70-fold diluted with water and poured onto a glass plate in amount of 5 mL per 100 cm$^2$. The mass fraction of silver in the solution used for preparation of gelatine films with embedded nanoparticles was 0.23 g L$^{-1}$.

To analyse the shape and determine the size of obtained silver nanoparticles, we studied their morphology by electron transmission microscopy using an LEO 912 AB Omega microscope and by scanning electron microscopy using an NVision 40-38-50 microscope. Figure 1 shows a typical electron diffraction pattern, which confirms that nanoparticles in the sample are single crystalline. The study of the morphology revealed the existence of flat nanocrystals of various shapes in the gelatine layer. An important synthesis quality criterion is the existence of a considerable amount of polygonal nanoprisms (inset in Fig. 1) and the absence of silver nanorods.

The mechanism of formation and subsequent growth of polygonal flat nanocrystals makes it possible to obtain single crystalline silver nanoparticles, which was confirmed by electron diffraction experiments.

The possibility to control the geometric dimensions and shape of synthesised flat silver nanocrystals makes it possible to obtain nanoparticles with a required absorption spectrum and thus optimise the selection of nanoparticles needed for different types of fibre lasers. The absorption spectrum of nanoparticles studied in this work is given in Fig. 2. It has a peak at a wavelength of 700 nm with the maximum optical density of 3.5. The position of the absorption maximum corresponding to the excitation of localised plasmons in a

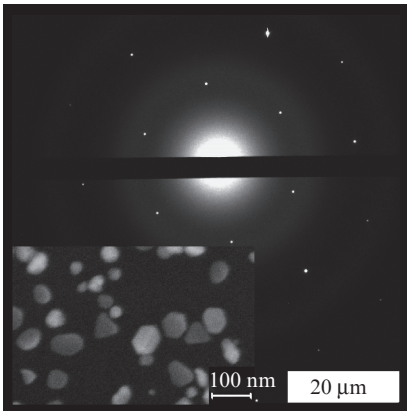


**Figure 1.** Diffraction pattern confirming that nanoparticles in the sample are single crystalline. The inset shows the SEM image of silver nanoparticles in the studied sample.

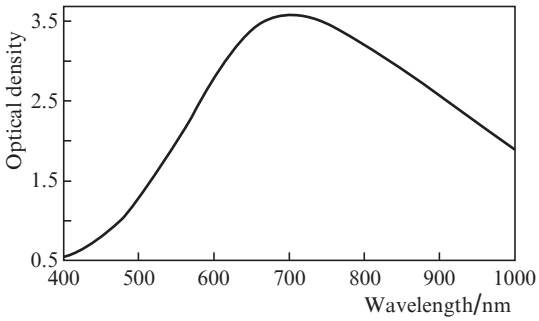


**Figure 2.** Absorption spectrum of the studied sample of flat nanoparticles in a photographic gelatine matrix.

nanoparticle strongly depends on its shape, which means that the broad absorption maximum of the studied sample is caused by the contribution of flat silver nanoparticles of different shapes. The sufficiently broad absorption spectrum of the sample allowed us to measure the nonlinear absorption at a wavelength of 785 nm using a femtosecond Ti:sapphire laser. It is important that the absorption at this wavelength is determined by the contribution of triangular flat silver nanoparticles, while the particles of other shapes have maxima at shorter wavelengths and almost do not contribute to the absorption at 785 nm.

The plasmon decay time in silver nanoparticles was measured by the pump–probe method with a pump wavelength of 392.5 nm and a probe wavelength of 785 nm. The pump wavelength determines not the possibility itself of plasmon excitation and electron subsystem heating, but affects only the efficiency of this process. The pump wavelength was chosen taking into account that the used power at this wavelength was sufficient for creating an excited plasmon state in nanoparticles, although the pump and probe intensities were relatively low with respect to the bleaching intensity. The interband absorption band in silver, whose long-wavelength edge (310 nm) lies at a much shorter wavelength than the pump wavelength used in this work, does not affect the absorption in nanoparticles. Note that the interband relaxation of the excited state occurs for characteristic times of the order of nanoseconds [5], which is considerably shorter than the characteristic times of the studied processes.

The experimental scheme used in this study is shown in Fig. 3. As a radiation source, we use a femtosecond laser pumped by a cw Verdi V10 laser with a wavelength of 532 nm. The second harmonic of the femtosecond laser is modulated by an acoustooptic modulator, passes through an automated optical delay line with a step of 0.156 μm, which corresponds to a time delay of 0.52 fs, and is used as a pump radiation. The probe radiation also passes through the delay line and is split into two beams with identical powers for recording on a balance photodetector, one of these beams passing through the same spot on the sample as the pump beam. The average pump power was 8 mW at a beam spot on the sample of 1 mm, the radiation power in the probing channel was 3 mW at a beam spot diameter of 0.5 mm, and the pulse repetition rate was 74 MHz. The pump radiation intensity in this case was chosen to be much lower than in the experiment on nonlinear absorption because the measurements must be performed in the regime of small perturbations of the studied sample. The pulse duration of the femtosecond Ti:sapphire laser did not exceed 100 fs. The frequency of the pump pulse

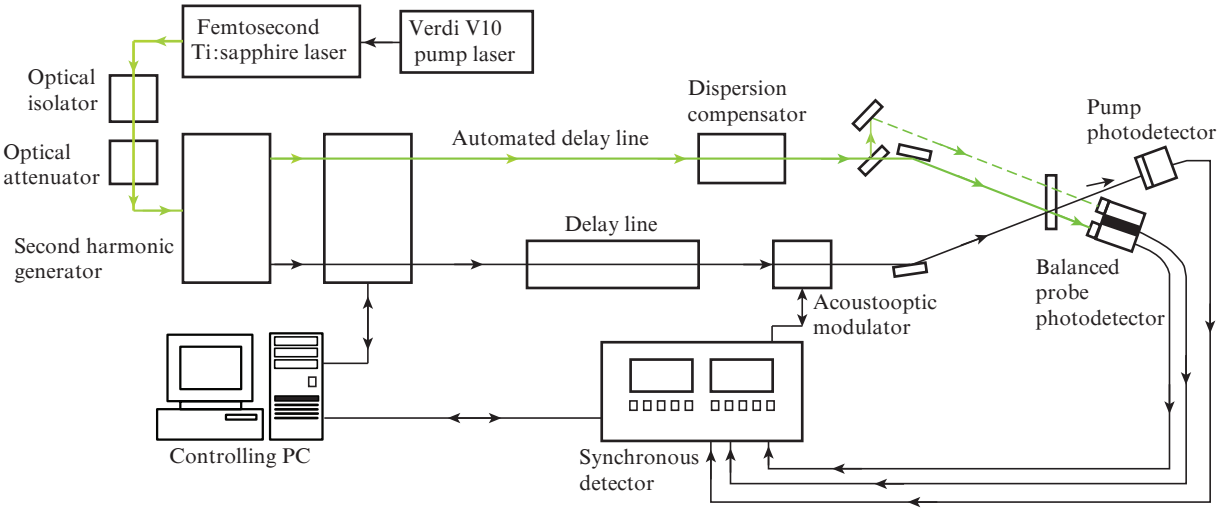


**Figure 3.** Scheme of the experimental setup for measuring the plasmon lifetime by the pump–probe method.

modulation by an acoustooptic modulator was chosen to be 86 KHz to minimise the noise. The amplified difference signal from the balance photodetector was detected by an SR-830 lock-in amplifier (synchronous detector) at the pump modulation frequency. The plasmon relaxation, which manifests itself in a decrease in transmission (Fig. 4), occurs for a characteristic time of ~2 ps, which allows one to use this material for generating picosecond pulses by passive *Q*-switching.

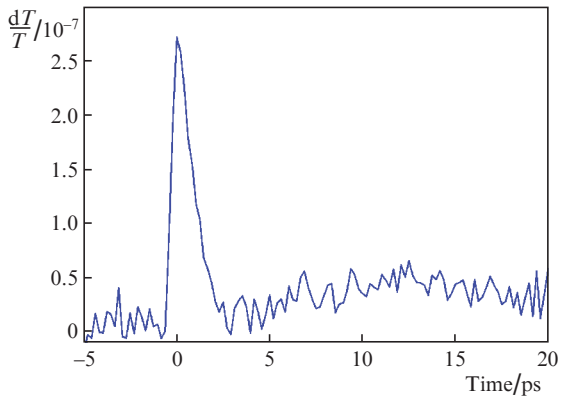


**Figure 4.** Plasmon relaxation in flat silver nanoparticles at a wavelength of 785 nm measured by the pump–probe method. *T* is the transmission coefficient of the sample.

The nonlinear absorption of the sample was studied by measuring the dependence of the optical transmission on the radiation intensity of a Ti:sapphire laser at a wavelength of 785 nm. The laser pulse duration in this case was 150 fs. The average power of the incident and output radiation was measured with a calibrated photodiode with an accuracy of ±1 μW. The nonlinear absorption curve in Fig. 5 shows that, with increasing pump radiation intensity to 10 MW cm$^{-2}$, the sample is bleached by 1.6 ± 0.07%. This makes it possible to use this material as a saturable absorber for passive mode locking in laser systems with a high radiation intensity typical for fibre lasers [6].

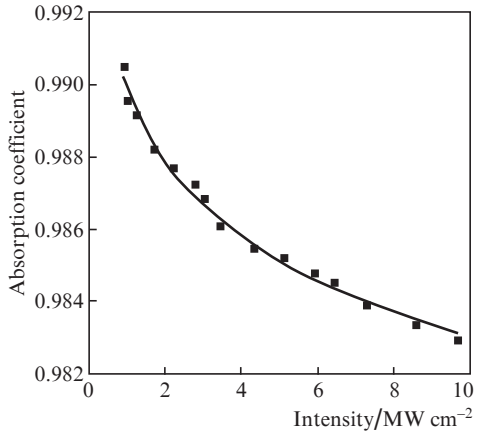


**Figure 5.** Dependence of the normalised absorption coefficient at a wavelength of 785 nm on the peak pump intensity for the studied silver nanoparticles in a photographic gelatine matrix.

It is believed that the nonlinear absorption in silver nanoparticles is related to short-time heating of the electron subsystem in the metal nanoparticle, which leads to a broadening of the plasmon resonance [7], and to a subsequent shift of the plasmon resonance to longer wavelengths [8].

Thus, we showed that the studied plane polygonal silver nanoparticles have the properties necessary for their application as saturable absorbers in passively mode-locked lasers, namely, they have nonlinear absorption with bleaching by 1.6 ± 0.07% at a pump intensity of 10 MW cm$^{-2}$ and the excited state lifetime of about 2 ps. The possibility of synthesising nanoparticles with absorption bands in different spectral regions allows one to use this type of materials in visible and near-IR lasers.

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