Physicochemical properties of submicron and nanoscale particles of Ga and AlGa alloy obtained by laser ablation in a liquid

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Abstract

Optical absorption spectra of gallium nanoparticles synthesized by laser ablation in 2-propanol, tetrahydrofuran, ethyl alcohol, liquid nitrogen and argon were obtained. A shift of the maximum and broadening of the absorption band of Ga, Al nanoparticles and AlGa alloy due to fast aggregation during the substitution cryogenic liquid in a colloid on the liquid at room temperature process were detected. When the AlGa nanoparticles were moved from the liquid argon medium to distilled water, a chemical reaction with the evolution of gaseous hydrogen was observed. The dependence of the evolved gas volume on the percentage ratio of metals in the AlGa film obtained by the vacuum deposition method was constructed. In the case of laser ablation of Ga in ethyl alcohol, the formation of gallium core / shell nanoparticles was fixed.

Keywords: laser ablation; nanoparticles; optical absorption spectra; gallium; thin films; cryogenic liquid; hydrogen

1. Introduction

At the present time, interest in gallium is due to its special chemical and physical properties, such as a strong tendency to form a Ga-Ga bond in solids and molecules, a low melting point of 303 K (29.8 °C), expansion of the volume upon freezing, and also the possibility of creating on its basis numerous technologically significant alloys and compounds [1]. The transition from macroscopic dimensions to nanoparticles leads to dependence of the melting temperature on the particle size - with decreasing diameter, the melting temperature also decreases [2]. The use of these properties can lead to the creation of logical information recording elements based on interphase transitions induced by optical radiation inside the gallium nanoparticle [3]. Gallium nanoparticles are the best option in terms of the energy required to change the phase state. Also, gallium can be used in alternative energy sources, as a component of the AlGa alloy, which prevents of the aluminum oxidation in the air medium. It is known, that the interaction of aluminum with water leads to the gaseous hydrogen emission, but under atmospheric conditions such a reaction is impossible, since oxidation of the aluminum surface occurs. The use of an oxidation resistant AlGa alloy is one of the ways to solve this problem [4]. The transition to alloyed nanoparticles can lead to an increase in the useful yield of the hydrogen evolution reaction by increasing the effective area of interaction of aluminum with distilled water.

One of the methods to obtain such nanoobjects is the method of laser ablation in liquid media. Unlike chemical methods, it is possible to obtain particles with a wide size distribution and completely free of the reaction products. In the case of chemical interaction of the target with the surrounding medium, laser radiation can initiate chemical processes. Therefore, it is promising to use inert cryogenic liquids.

The change in one of the parameters of laser ablation (the source of laser radiation, the target or the liquid in which the process takes place) will affect on the final products. The formation of nanoparticles and differences in their form, size and degree of aggregation can be registered by using absorption spectra.

Therefore, the aim of this work was to determine the effect of the liquid medium in which the ablation takes place on the optical properties of gallium nanoparticles and also to consider changes in optical spectra associated with the rapid aggregation of Ga, Al nanoparticles and AlGa alloy during the substitution in a colloid of a cryogenic liquid (liquid nitrogen) to a liquid at room temperature.

2. Experimental technique

For the synthesis of nanoparticles, a standard scheme of the laser ablation method in liquid, supplemented with a special cuvette for working with liquid nitrogen or argon, which prevents the liquid from boiling around the target, was used [5]. The radiation of an Nd: YAG laser with a wavelength of 1064 nm, a pulse repetition rate of 20 Hz, and pulse duration of 250 ps was focused on the target surface. As liquids were used: glycerol, ethyl alcohol, 2-propanol, tetrahydrofuran, liquid nitrogen and liquid argon. The thickness of the liquid layer above the target surface was 5 mm. Surface treatment took place both in a stationary mode - laser radiation was focused at one point of the target, and in the scanning mode - a cuvette with a sample, by means of motorized tables Standa moved relative to the stationary laser beam. For the analysis of obtained particles by scanning electron microscopy, a titanium foil was placed in the cuvette with the target during irradiation to precipitate the ablation products.

The obtained colloids were analyzed by the LOMO spectrophotometer SF-56. The measurement range is 190-1100 nm, the spectral resolution is 0.3 nm. Since the design of this instrument does not provide for the analysis of cryogenic sols, in both parts of the experiment a technique for replacing cryogenic liquid in a colloid with a liquid at room temperature was used [6].

The first series of experiments consisted in obtaining colloids of gallium particles to further determine the optical absorption spectra associated with plasmon resonance. The target was a plate of gallium (99.99%) 2 mm thick. The energy of laser radiation in the pulse was 15 mJ, and the laser fluence varied from 20 to 400 J / cm^2. Irradiation was performed in a stationary mode for 30 minutes.

To compare the optical characteristics of Ga nanoparticles obtained by laser ablation with the optical characteristics of gallium particles synthesized by other methods [7, 8], glycerol, distilled water, ethyl alcohol and isopropyl alcohols were used as liquid media. However, at laser ablation in room temperature fluids the probability of formation of microaggregates from gallium nanoparticles increases. This is due to the fact that the melting temperature of the target is close enough to room temperature and the removed material does not have time to crystallize. Therefore, the next stage was the use of liquid nitrogen. In [6], differences in the formation of a liquid nitrogen colloid droplet during the overflow into cuvettes filled with different liquids were shown. Therefore, in this work, the colloid of Ga nanoparticles was divided into two equal volumes, after which one part was transferred to ethyl alcohol and the other to be compared to isopropyl alcohol.

In the second series of experiments, a thin AlGa film was ablated in liquid nitrogen and liquid argon media. The production of this film was carried out using a vacuum universal station (VUS-5), by spraying aluminum (99.99%) and gallium (99.99%) onto the surface of the slide. As vaporizers, graphite rods were chosen. On the evaporators aluminum and gallium in the proportions determined by laboratory scales Electronic balance B 2104 were placed:

- 99% Al, 1% Ga
- 97% Al, 3% Ga
- 95% Al, 5% Ga
- 93% Al, 7% Ga
- 90% Al, 10% Ga

The energy of laser radiation in a single pulse was 0.3 mJ, and the laser fluence at the samples surface was 0.11 J / cm^2. It was selected in such a way that the glass substrate did not break down. Irradiation occurred in the scanning mode. The treatment area was 30 mm^2. To compare the optical absorption spectra of alloyed AlGa nanoparticles obtained in liquid nitrogen or liquid argon, the particles were transferred to distilled water.

In the same way, a thin aluminum film and a thin gallium film were prepared and irradiated in a liquid argon medium, followed by the replacement of argon in the colloid by H_2O.

Visualization and elemental analysis of ablation products deposited on the titanium foil from the colloid were carried out using a scanning electron microscope Carl Zeiss Evo 50 equipped with a nitrogen-free energy dispersive detector X-Max 80 (EDX).

3. Results and discussion

Figure 1a shows the absorption spectra of gallium nanoparticles obtained by laser ablation in ethyl and isopropyl alcohols. It can be seen that the spectra have the same absorption band in the region from 262 to 280 nm with local peaks at 267 and 275 nm. This can be attributed to the fact that both liquids have practically the same density - 789 and 786 kg / m^3, respectively. According to the published data [7], this parameter of the medium has a significant effect on the optical properties of metallic nanoparticles. It is important to note that the absorption lines of gallium particles synthesized in isopropyl alcohol are shifted to the long-wavelength region of the spectrum in the present paper in compare with the data obtained in [7].

The spectra of nanoparticles obtained in glycerol and water are characterized by a broad absorption band. In the case of glycerol, this may be due to the formation of aggregates of nanoparticles in a viscous medium. And the process of ablation in water is characterized by the formation of oxides. In alcohols, the absorption band is much narrower. This difference can be explained by the fact that due to the high activity of the surface of the metallic particles, they bind to the solvent molecules. This leads to decrease of the particles aggregation probability. In glycerol, the absorption band of 220-300 nm is characterized by two absorption maxima at 224 nm and 260 nm, respectively. In water, the absorption band is shifted by 245-307 nm due to oxidation and has a maximum at 272 nm.

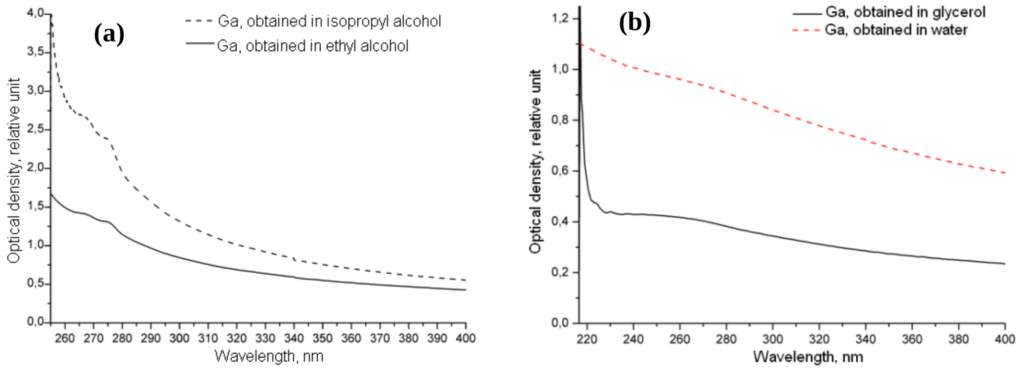

Fig.1. The absorption spectra of gallium nanoparticles obtained **(a)** in isopropyl and ethyl alcohol; **(b)** in glycerol and distilled water.

By scanning electron microscopy of gallium particles obtained in ethyl alcohol spherical structures with characteristic dimensions from 80 to 800 nm were revealed. In a number of cases, elongated shape gallium structures with a thickness of 50 to 100 nm, repeating the contours of the particles, were found on the titanium foil surface. Apparently, such structures are fragments of the shell of nanoparticles. The formation of such structures is most often associated with the formation of bubbles at the interaction of laser radiation with the target [9, 10].

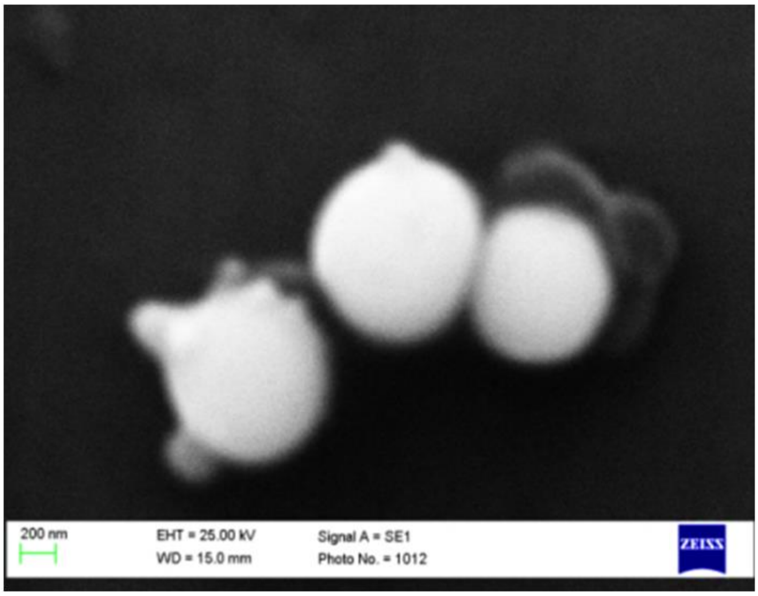

Fig.2. SEM image of gallium particles obtained by laser ablation in ethyl alcohol.

Figure 3 shows the absorption spectra of Ga nanoparticles obtained in liquid nitrogen. The colloid was divided into two volumes. In the first volume, the cryogenic liquid was replaced by isopropyl alcohol, and in the second - by ethanol. In the case of replacement with isopropyl alcohol, the absorption band falls on the interval 215-290 nm with maxima at 231 and 280 nm. And when substituted for ethanol, the absorption band (205-280 nm) and its maxima (212 and 248 nm) are shifted to the short-wavelength region of the spectrum.

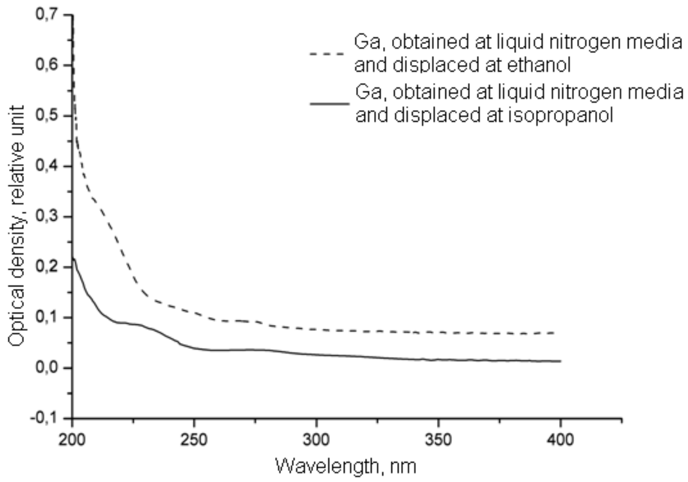

Fig.3. Absorption spectra of Ga nanoparticles obtained in liquid nitrogen and transferred to isopropyl and ethyl alcohols.

SEM - analysis of the initial target in the form of the thin AlGa film, obtained by the vacuum deposition method, is shown in Fig. 4. The film thickness was 600 nm. The evaporation temperature of Ga is 2420 °C, and the evaporation temperature of Al is 2380 °C. However, it should be noted that at the initial moment of deposition of metals on the glass substrate surface, the gallium concentration exceeds the concentration of aluminum. On the evaporation process may influence the presence on Al of an oxide film, whose evaporation temperature is 3000 °C.

A comparison of the optical absorption spectra of alloyed AlGa nanoparticles obtained in liquid nitrogen and liquid argon is presented on Figure 5. For this, cryogenic liquids in colloids were replaced by distilled water. In both cases, an absorption band from 210 to 300 nm with peaks at 224 and 267 nm is observed. The difference in spectra lies in the fact that the particles obtained in the liquid nitrogen medium have one more, broad, absorption band in the range from 300 to 700 nm.

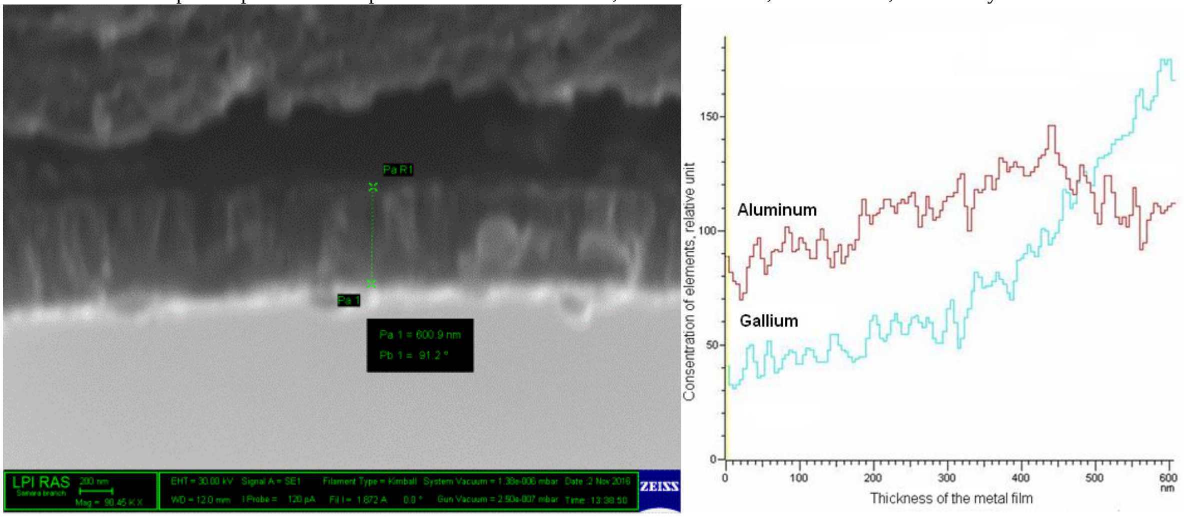

Fig.4. SEM-image and elemental analysis of the thin AlGa film by the thickness.

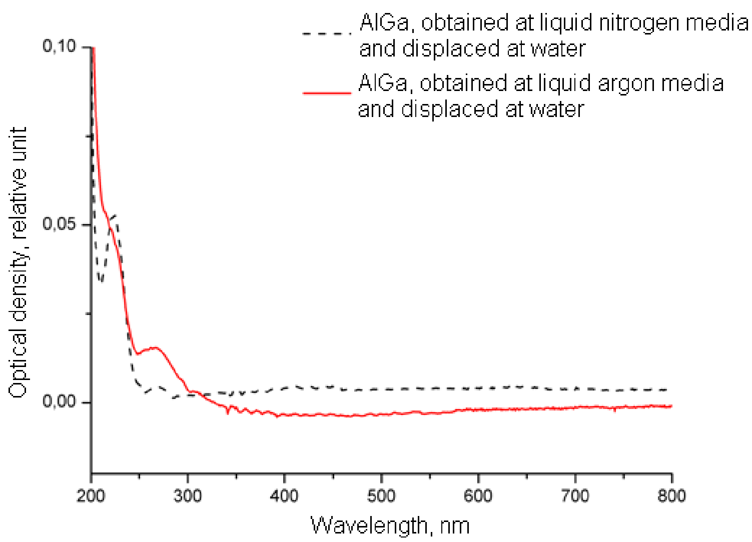

Fig.5. Absorption spectra of AlGa nanoparticles obtained in liquid nitrogen and liquid argon, replaced in water.

During the replacement of AlGa nanoparticles from liquid argon to water, active gas evolution was observed. When the open flame was brought on, a rapid ignition of the gas with a characteristic pat was occurred. Therefore, it can be argued that hydrogen gas is released as a result of the chemical reaction $2Al + 6H_2O = 2Al(OH)_3 + 3H_2$. Nanoparticles of Al synthesized in liquid nitrogen and transferred to water do not enter into this reaction, since, apparently, the formation of aluminum nitride occurs.

Figure 6a shows a comparison of the absorption spectra of AlGa nanoparticles obtained in liquid argon during the ablation of thin films with different percentages of metals, after being replaced by water. With a change in the composition of the film, the absorption bands and their maxima remain the same, only small changes in the optical density are observed. The maximum optical density was recorded for 95% Al and 5% Ga. The dependence of the volume of the evolved gas on the percentage of metals in the target is shown in Fig. 6b. The greatest volume of gas yield, 8 milliliters, is accounted for 95 percent of aluminum and 5 percent of gallium.

Absorption spectra of Al and Ga nanoparticles obtained in a liquid argon medium after the replacement of argon in a colloid by H_2O are shown in Figure 7. Aluminum nanoparticles have an absorption band from 210 to 250 nm, and gallium particles have an absorption band from 250 to 300 nm.

By using a scanning electron microscope, images and an elemental analysis of micron and submicron particles synthesized in liquid argon and liquid nitrogen during the ablation of thin AlGa films with followed replacement of the cryogenic liquid in the colloid on water were obtained. According to elemental analysis, the presence of both gallium and aluminum was found in the composition of nanoparticles (Fig. 8a, b). The presence of nitrogen on the spectrum in the case of ablation in liquid nitrogen indicates the possible formation of nitrides of the used metals.

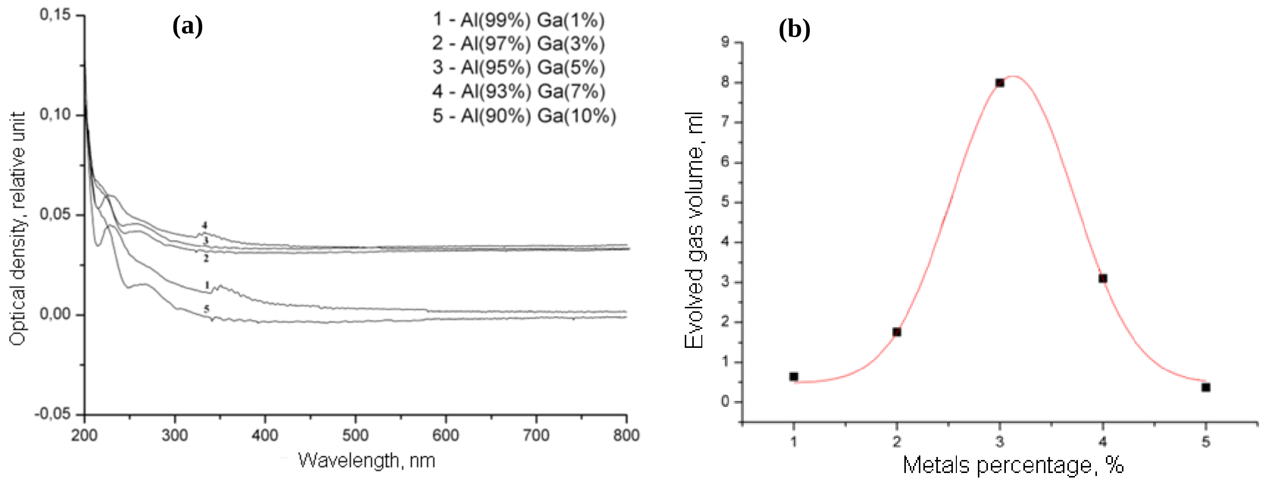

Fig.6. (a) Absorption spectra of AlGa nanoparticles obtained in liquid argon during the ablation of thin films with different percentages of metals after the replacement of argon by the water; (b) Graph of the dependence of the evolved hydrogen volume on the percentage ratio of metals in the target.

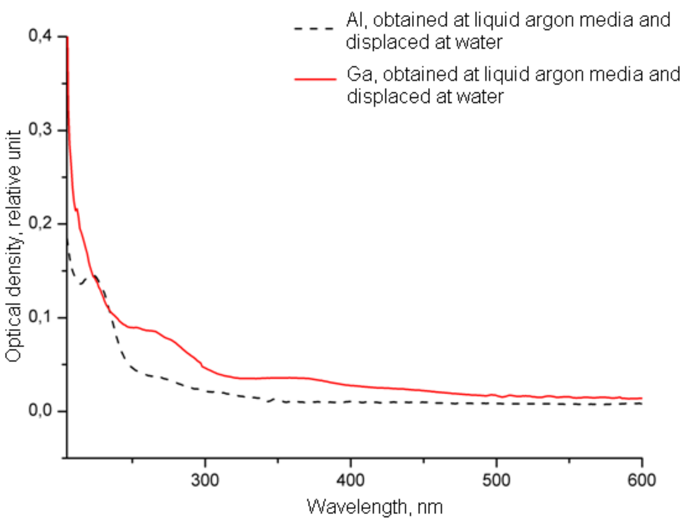

Fig.7. Optical absorption spectra of Al and Ga nanoparticles obtained in a liquid argon medium with followed argon replacement in a colloid on H2O.

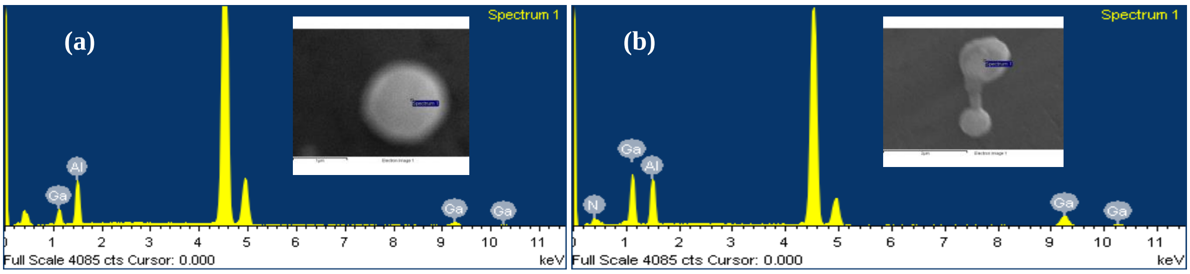

Fig.8. Data of the energy-dispersion analysis of micron and submicron nanoparticles obtained by laser ablation of AlGa target **(a)** in a liquid argon medium, **(b)** in a liquid nitrogen medium with followed replacement in a colloid of a cryogenic liquid on water.

4. Conclusion

In the present work, micro- and nanoparticles Ga, Al, AlGa by laser ablation in liquid media were synthesized. Shell fragments of gallium particles were found. Optical absorption spectra of Ga nanoparticles obtained in glycerol, water, isopropyl alcohol, ethanol and liquid nitrogen are shown. In the case of liquid nitrogen, the absorption spectra of the particles were obtained after replacing the cryogenic liquid on isopropyl and ethyl alcohols. The absorption spectra of AlGa particles synthesized in liquid argon and liquid nitrogen were also obtained. Information about the optical absorption spectra of Ga nanoparticles obtained at various parameters is promising from the point of view of creating gallium logic information recording elements [3].

The technique proposed for applying thin AlGa films that are not oxidized in air and their further laser ablation in an inert cryogenic liquid can be used in the development of alternative methods for producing hydrogen. The optimal percentage of Al and Ga in the composition of these films (19: 1) was selected, at which the maximum yield of hydrogen gas was observed after irradiation in liquid argon with following replacement on water.

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