Laser formation of nano-Si structures in glasses

E S Babich, A V Redkov, V G Melehin, D Khlopin, and A A Lipovskii

1Peter the Great St. Petersburg Polytechnic University, St. Petersburg 195251, Russia
2Institute of Problems of Mechanical Engineering, St. Petersburg 199178, Russia
3A. F. Ioffe Physical-Technical Institute, St. Petersburg, 194021, Russia
4Université de Technologie de Troyes, 10004 Troyes Cedex, France
5Alferov University, St. Petersburg 194021, Russia

Abstract. The irradiation of a BOROFLOAT® 33 glass plate with lithographically-fabricated array of aluminum nanodisks on the surface by a focused low-power 523 nm laser beam resulted in the formation of silicon nanocrystals in the subsurface layer of the glass. The nano-Si was registered with Raman scattering technique. The formation of the nano-Si is local and grown nanocrystals are stable.

1. Introduction
As known, metal nanostructures can initiate crystallization of amorphous silicon and germanium, which allows essential decreasing of the crystallization temperature [1–3]. It is also known that silicon nanoparticles can be formed in glasses under the irradiation by intensive high-energy electron beam [4–6]. The typical process of the nanoparticles formation includes the formation of silicon-in-glass oversaturated solid solution (because of oxygen loss) and its subsequent phase decomposition either directly in the course of electron irradiation or after additional heat treatment [4–8]. Under sufficiently high temperature and long duration of the processing, these nanoparticles become crystalline. In this paper, we demonstrate for the first time the formation of Si nanocrystals (nano-Si) which growth is provided by the exposition of lithographic metal nanostructures by a low-power laser.

2. Experimental
We have fabricated a square array of 200 nm in diameter and 40 nm in height aluminum disks with 300 nm periodicity on the surface of a 500-μm thick borosilicate (BOROFLOAT® 33) glass plate purchased from Agar Scientific. Aluminum nanodisks were fabricated using a standard electron beam lithography on Raith e-Line setup. Parameters of the electron gun were 20 kV accelerating voltage, 30 pA electron current, 2-4 nm beam width, and 0.3-0.7 mC/cm² range of exposing charge density (or dose) was used. E-beam writing was done on a 120 nm thick layer of poly(methyl metacrylate) (PMMA). After the evaporation of a 40 nm layer of aluminum, the development continued with lift-off process in acetone. Fabricated structure has been illuminated by a CW 532 nm laser using 100x/0.9 and 10x/0.25 objectives, which provided 18 mW and 33 mW maximal laser power at the sample surface, respectively. The laser irradiation and Raman characterization of the irradiated samples were made with the confocal Raman microscope Witec Alpha 300R.

In Figure 1a, b we present an optical microscope image of the laser-exposed sample surface and the results of the mapping of the Raman peak at 515 cm⁻¹ (Si optical phonon). The results of the mapping present the distribution of the integral intensity of 70 cm⁻¹ wide Raman peak in the vicinity of 515 cm⁻¹. It is seen in Figure 1a that the light reflection has changed in the irradiated area. The
mapping, which was carried out after the laser irradiation, reproduces the geometry of the laser-exposed area (compare Figures 1a and 1b).

Figure 1. (a) Microscopic image of the glass with the array of Al nanodisks, (b) corresponding Raman map (mapping with 100x/0.9 objective, 0.3 μm step, 18 mW incident laser power and 0.5 s acquisition time in each point) of integral intensity of nano-Si peak at 515 cm⁻¹, (c) the image of the specimen, where nanodisks were removed prior the laser irradiation, and (d) corresponding Raman map (mapping with 10x/0.25 objective, 1 μm step, 32.8 mW incident laser power and 0.14 s acquisition time in each point) of 515 cm⁻¹ line and averaged Raman spectra measured in the laser-exposed area (e) and out of this area (f).

The data presented in Figures 1a-b evidence the formation of nanocrystalline silicon in the region of the aluminum nanodisks array, which was irradiated with the laser beam. The maps presented in Figures 1c-d also show that the laser irradiation of the glass surface from which the disks were removed before the laser exposition did not resulted in the appearance of the nano-Si Raman line. This means that the effect of the laser treatment (even under the maximal power of the laser) is not sufficient for the growing of silicon nanocrystals in the absence of Al nanodisks, and the role of the aluminum nanostructures is crucial in the formation of the nano-Si. In Figures 1e, f averaged over 4 measurements Raman spectra of the irradiated and non-irradiated regions are presented. The Raman spectrum presented in Figure 1e is a typical one for nano-Si [9,10] with the peak near 515 cm⁻¹. The measurements of Raman spectra in laser-exposed region of the sample after its keeping for two months under room conditions have also shown the existence of the scattering peak corresponding to nano-Si (Figure 2). This allows concluding about stability of the nanocrystals at least for this period.

3. Discussion
Our Raman scattering measurements show that the lateral dimension of the subsurface glass region containing the nanocrystals is about of the lateral size of the aluminum nanodisk. Supposedly, the heat transfer from the nanodisks to glass matrix is sufficient to activate formation of silicon via
aluminothermic reaction [11]. The latter results in the formation of critical nuclei and the growth of nano-Si indicated by our Raman measurements.

**Figure 2.** (a) Microscopic image of the glass surface with the array of Al nanodisks and (b) the map of the integral intensity of 515 cm\(^{-1}\) Raman line. The marked areas were exposed with the laser two months before the mapping, which is performed using 10x/0.25 objective with 0.2 µm step, the incident laser power at the sample surface is 33 mW, the acquisition time is 1 s in each point.

We tried to evaluate the maximal size of the formed silicon nanocrystals and the thickness of the subsurface glass layer enriched with the nanocrystals. For this, we performed a series of long, 100 seconds and more, laser irradiations of the specimen in one point. The minimal Si phonon frequency registered in the irradiated point was 507 cm\(^{-1}\). This corresponds to silicon nanocrystals not exceeding 10 nm in diameter [12] in case their temperature does not significantly exceed the activation temperature of the aluminothermic reaction (660°C [11]) provided by the laser irradiation. This evaluation of the temperature is close in the order of magnitude to the results of modeling presented in Ref. 13 with the account for the power of our laser, up to ~33 mW. In Ref. 13 the increase in temperature ~16°C per one mW of laser power was predicted for 800 nm square aluminum nanostructures. Besides, at this temperature one can neglect the shift of the Raman peak, which can be induced by mechanical stress in the nano-Si induced by the glass matrix, because of the low (<13 poise) viscosity of the glass at temperatures exceeding 560°C [14].

We also performed COMSOL® simulation of the temperature distribution under a hot, 660°C, aluminum nanodisk placed on the glass surface. It shows that the thickness of the glass layer, which temperature exceeds ~600°C, is in the range of several tens of nanometers. This thickness should correspond to the glass layer enriched with Si nanocrystals considering the low diffusivity of silicon and fast decrease of the glass temperature when moving away from the glass surface.

### 4. Conclusion

We have demonstrated that the conventional low energy e-beam lithographic formation of a given aluminum nanostructures followed by exposing the nanostructures by focused lower-power laser beam can be used for the fabrication of prescribed stable 2D structure of silicon nanocrystals. Evaluated average size of the nanocrystals is in the range below 10 nm.

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