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Obtaining a porous surface on germanium by exposure to infrared nanosecond laser pulses

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The creation of porous structures on the surface of monocrystalline germanium is considered in order to change the values of reflection coefficients, reflection indicators, and surface preparation for diffusion welding. For this purpose, exposure to powerful pulses of a nanosecond IR laser in an aqueous medium was used. It is shown that in this way it is possible to create separate sections with a porous structure with a pore size from fractions to 10 microns on the surface of monocrystalline germanium. The optimal pulse energy density is of the order of 30 J/cm^2.

Keywords: germanium (Ge), nanosecond laser, aqueous medium, porous surface, diffusion welding.

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Introduction

When exposed to an intense laser pulse, pores may appear in transparent materials due to the selective interaction of radiation with absorbing centers [1,2]. It is also possible to create a porous structure on the surfaces of opaque materials as a result of boiling the melt and its rapid cooling [3].

The creation of porous structures on a number of semiconductor electronics and optics products is important in order to change the values of reflection coefficients, reflection indicators, and some other characteristics. In particular, porous silicon has shown its effectiveness in photoelectronic converters. Due to the porous structure of the surface, it was possible to reduce reflection losses, which increased the efficiency of solar panels [4]. Since the effective surface area on a porous surface increases significantly, and, consequently, its energy characteristics, porous germanium has proved promising for lithium-ion battery anodes, as well as for solar energy [5]. A porous surface may also be of interest in the deposition, adhesion of impurities or films in the production of heterostructures and other structural materials [6].

There are several methods for obtaining a porous surface on Ge [7–13]. These are methods of ion implantation, thermal and chemical etching, and exposure to frequency-pulse laser radiation. These methods have their advantages and disadvantages. In particular, to prepare a germanium window before diffusion welding, it is necessary to create a porous structure only on its edge, without damaging the optical surface. The existing chemical and thermal etching methods [8–11], although they make it possible to obtain a porous structure on Ge, but it is formed on the entire surface of the sample; there is also a possibility of contamination and damage to the optical surface.

It is reported in this paper that local areas of a porous structure on the polished surface of a Ge single crystal are obtained as a result of exposure to pulsed IR radiation from a nanosecond Nd:YAG laser in an aqueous medium.

Experimental methodology

The experiment was carried out in laboratory conditions at a temperature of 22°–25°C and at normal atmospheric pressure.

Industrial samples of GMO grade monocrystalline germanium n, a type with electrical resistivity $\sim 5\,\Omega\cdot$cm, doped with antimony (its concentration $\sim 3\cdot 10^{14}\,\text{cm}^{-3}$), were used. The sample surfaces corresponded to the crystallographic planes $\{111\}$ with an accuracy of < 10 min. The surface of the samples was optically treated using the chemical-mechanical method [14].

The Nd:YAG laser was used for exposure to laser radiation (wavelength $\lambda = 1.064\,\mu$m, pulse duration $\tau = 10$ ns, pulse energy up to 0.6 J, pulse repetition rate up to 10 Hz,

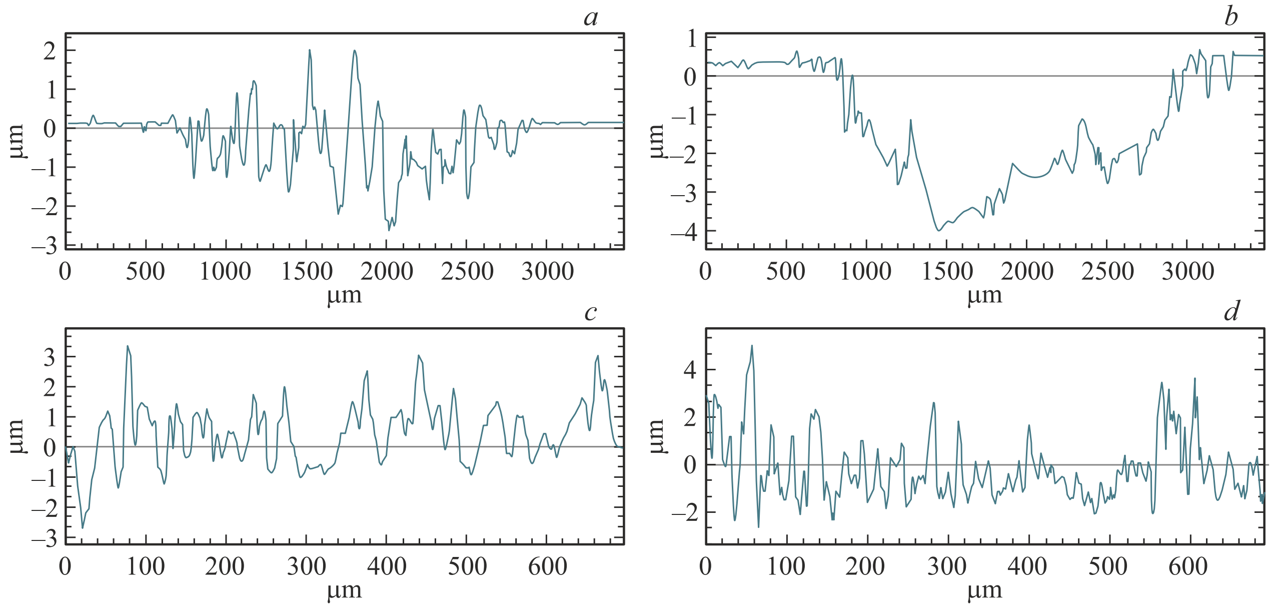

Figure 1. 2D profile charts of the surface of a Ge single crystal obtained after exposure to a pulse of laser radiation with an energy density of Wp = 32 J/cm^2: *a*) in the air and *b*) in the water when using a lens with a ×2 magnification; *c*) in the air and *d*) in the water when using a lens with a ×20 magnification.

divergence 16 mrad) [14]. The radiation was concentrated on the sample surface into a spot 1.5 mm in size using a quartz lens with a focal length of 500 mm. The technique of laser exposure is described in detail in Ref. [15].

The radiation energy density Wp on the sample surface varied in the range 20–32 J/cm^2, which is significantly higher than the optical breakdown threshold for the germanium regime under consideration. However, it was not possible to create a pore formation mode during the experiment in an air environment (Figure 1). Then, the light-hydraulic effect was used to increase the effectiveness of radiation exposure to the sample surface, which was first discovered in the laboratory of A.M. Prokhorov [16]. During an optical breakdown on the surface of a material located in a liquid, the effect of the mechanical pulse of the plasma torch on the surface is enhanced due to the fact that the liquid restricts the spread of the laser plasma.

To conduct experiments before exposure to laser radiation, cylindrical (diameter 28 mm and thickness 30 mm) samples of Ge were placed in a cuvette with deionized water (OST 11.029.003-80). After exposure, the optical stability of water decreased markedly due to the appearance of a significant number of ablated germanium particles [17]. Since the Ge surface was irradiated in a horizontal position, a reflecting mirror (at an angle of 45°) was located directly after the lens. To protect the optical elements from splashes of water formed when exposed to laser radiation, the cuvette with the sample was covered with a transparent quartz plate. Before each launch, the portion of deionized water in the cell was completely replaced. The water layer above the sample surface was maintained at the level of ∼ 1 mm.

Before and after exposure to laser radiation, the sample surface was monitored using a NewView 7300 optical profilometer, as well as a JEOL JSM 6610LV scanning electron microscope (SEM).

Experimental results and discussion

The creation of porous structures on the surface of Ge was studied in this paper for intensifying the processes of diffusion welding [18]. One of the important applications of monocrystalline germanium in IR optics [19] are sealed windows of photodetector devices that operate most efficiently at cryogenic temperatures. Typically, entrance germanium windows with an already applied antireflection coating are welded to a quartz cryostat bulb with a photodetector cooled to a temperature of liquid nitrogen (and in some cases helium) by diffusion welding [20].

An effective mode of pore formation on the surface of an opaque material was demonstrated in Ref. [3] as a result of exposure to a femtosecond laser pulse. The mechanism of the porous structure formation is explained. The molten metal surface layer boils during the pulse action and cools quickly after the pulse ends. According to the authors of this article, a similar process occurs on the surface of monocrystalline Ge.

A simpler and more technologically advanced nanosecond laser was used in this study. Such lasers are mass-produced and are actively used in various branches of science and technology, as they are much cheaper and their operation is much easier than femtosecond lasers.

Figure 1 shows 2D profile charts of the surface of a single crystal Ge, obtained after exposure to a pulse of radiation

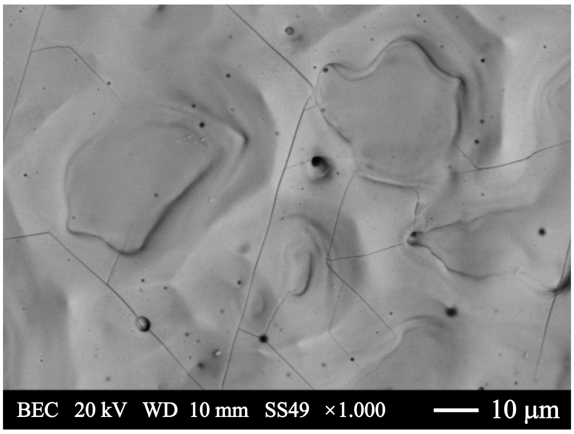

Figure 2. The surface of a Ge (SEM) single crystal after exposure to a pulse of Nd:YAG laser radiation ($\lambda = 1.064\,\mu$m, $\tau = 10$ ns, $\mathrm{Wp} = 32\,\mathrm{J/cm^2}$) in the air.

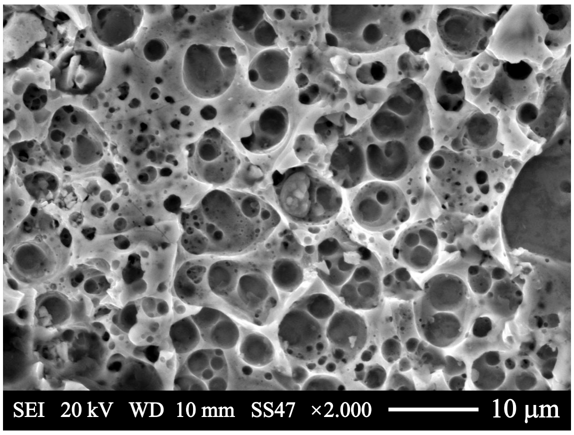

Figure 3. SEM image of the Ge single crystal surface after exposure to a pulse of Nd:YAG laser radiation ($\lambda = 1.064\,\mu$m, $\tau = 10$ ns, $\mathrm{Wp} = 32\,\mathrm{J/cm^2}$) in the water.

with an energy density of $\mathrm{Wp} = 32\,\mathrm{J/cm^2}$; a) in air and b) in water — at a two-fold magnification; c) in air and d) in water — at a twentyfold magnification.

It is clearly seen that the surface roughness of monocrystalline Ge increased sharply when exposed to laser radiation in the air in the irradiated area (the range of peaks and troughs reached $2\,\mu$m), however, pronounced cratering and pore formation is not observed. Figure 2 shows the surface of a Ge single crystal obtained using SEM is shown after exposure to a pulse of Nd:YAG laser radiation ($\lambda = 1.064\,\mu$m, $\tau = 10$ ns, Wp $=32\,\mathrm{J/cm^2}$ in the air environment. It is clearly seen that in this case, although there is melting, but the pores are almost not observed. At the same time, cracks were formed on the surface.

When radiation is applied to the same sample in an aqueous environment, the picture changes dramatically. A clearly visible crater appeared in the irradiated zone, with a depth of more than $4\,\mu$m. Figure 3 shows an image (SEM) of the surface of a Ge single crystal after exposure to a pulse of radiation from the same laser, and under the same exposure conditions, but in an aqueous environment. It is clearly seen that the irradiated crystal surface is dotted with a porous layer. The size of the formed pores ranges from fractions of micrometers, up to $5-10\,\mu$m.

Based on the formula for the depth of thermal penetration $l = \sqrt{\alpha\tau}$, the thickness of the germanium layer heated to boiling point when exposed to a laser pulse with $\tau = 10$ ns is estimated as ~ 590 nm. However, in the aquatic environment, the cooling process after the end of the radiation pulse occurs significantly faster than in the air. Therefore, the heated surface layer freezes before it has time to transition from a partially vapor phase to a liquid one. The thickness of the porous layer $\sim 1.5-2.5\,\mu$m is estimated in advance by the size of the formed pores (Figure 3). In the future, we propose to study this layer more precisely by controlling the thickness on the chipped samples using SEM.

Modification of the surface of the parts to be welded by laser pulses makes it possible to reduce the temperature and duration of the welding process [18], which is extremely important for the problem under consideration. Indeed, for Ge, as a semiconductor, an increase in temperature leads to a decrease in optical transmission due to impurities both appearing during chemical interaction with the environment and due to the diffusion of coating atoms.

The conditions of use of the photodetector assume a rigid focusing of the studied radiation on its surface. This eliminates the use of a window with a porous optical surface due to the intense pore scattering. The use of laser exposure makes it possible to obtain a porous structure on a predetermined area of the surface of a Ge monocrystalline sample, and the use of a mask makes it possible to eliminate laser damage to the optical region. For the purpose of leveling crater formation when exposed to a laser pulse on the surface of a monocrystalline Ge. The radiation is supposed to be applied in the „snake“ mode, with 30% overlap of the laser spots [21]. In this case, it is possible to maintain the height difference allowed for diffusion welding on the surface of the window from Ge.

Conclusion

A porous structure is formed on the germanium window fragment, which does not affect the optically processed rest of the window sample surface. The energy density of a laser pulse for obtaining a porous surface on a monocrystalline Ge, which is $20-32\,\mathrm{J/cm^2}$, has been experimentally determined. The obtained result allows us to count on the successful continuation of work on diffusion welding of a monocrystalline germanium window with a photodetector cryostat.

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Conflict of interest

The authors declare that they have no conflict of interest.

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