Applied Physics A (2018) 124:595
https://doi.org/10.1007/s00339-018-2010-x

Applied Physics A
Materials Science & Processing

Hydrogen in optical germanium and reduction of its negative impact on the crystal properties by ultrasonic processing

G. S. Pekar[1] · A. F. Singaevsky[1] · M. M. Lokshin[1] · A. A. Singaevsky[1]

Received: 19 June 2018 / Accepted: 3 August 2018

Abstract
Hydrogen content and its effect on the properties of optical germanium has been first investigated. Large coarse-grained plates of Na-doped optical germanium, grown in an inert atmosphere, are shown to contain dissolved hydrogen in a concentration about 1.9×10^{17} cm^{-3}. It is shown that the presence of hydrogen can lead to the porosity of the plates, to the plate cracking and to the release of toxic gases during plate machining, as well as to some other negative effects. A technique for ultrasonic plate processing has been developed, which leads to a decrease in the hydrogen content by about 7 times, to an increase in the mechanical strength of the plates, to an increase in the material density, to a decrease in the Ge lattice parameter, and ultimately to eliminating all listed negative effects caused by the presence of hydrogen. The developed method of plate processing has found a successful application in the industrial production of protective screens for thermal imaging systems of night vision based on optical germanium plates.

1 Introduction

The role and properties of hydrogen in germanium have been studied for a number of years primarily in single crystals of high-purity germanium used for production of gamma-ray detectors [1–3]. Those crystals were grown in a hydrogen ambient and contained trapped hydrogen at a concentration 10^{14}–10^{15} cm^{-3} [2]. In such studies, the focus was on the charge state of this impurity, its location in the germanium lattice, interactions with various impurities and defects, etc. As for optical germanium, the presence of hydrogen in the crystals and its effect on crystal properties remains unexplored, a fortiori that such crystals are usually grown in a gaseous medium that does not contain hydrogen. However, as shown in this paper, such an effect exists and can lead to unforeseen results.

At present, optical germanium is used, among other applications, for manufacturing large-area windows (screens) that protect thermal imaging systems of night vision from external influences, such as atmospheric precipitation, dust, etc. The linear dimensions of protective screens can exceed 30 cm. Since the commercial growth of single crystals of such dimensions is unreasonable due to technical difficulties and high cost, the screens are usually manufactured of polycrystalline optical germanium plates doped with Sb. The optical parameters of such plates are mostly inferior to the parameters of single crystals. As a rule, the polycrystalline plates have lower transmittance, greater dispersion and a significant heterogeneity of characteristics over the plate area. The deterioration of the optical characteristics of polycrystalline germanium is largely due to more favorable conditions for the formation of so-called clouds of impurities [4], whose dimensions are comparable with the wavelength of the incident infrared radiation [5]. It leads to a substantial scattering of this radiation as it passes through the polycrystalline sample.

Such difference between the parameters of single-crystalline and polycrystalline germanium screens is small or even absent in cases when the screens are made of large-grain polycrystalline plates of Na-doped optical germanium (Ge:Na). The Na-doped optical germanium was proposed by us previously [6, 7], and a technique for its growing in the form both of single crystals and of polycrystalline plates with an area of up to 500 cm^2 was developed. It was shown that the formation of impurity clouds in Ge:Na is unlikely [8] and the optical parameters of coarse-grain polycrystalline samples practically coincide with those of Ge:Na single crystals. As a result, the polycrystalline Ge:Na protective

✉ G. S. Pekar
pekar@isp.kiev.ua; gpekar1@gmail.com

[1] V. Lashkaryov Institute of Semiconductor Physics, National Academy of Sciences of Ukraine, 41 Prospect Nauki, Kiev 03028, Ukraine

Published online: 10 August 2018

screens and windows have found a successful practical application.

When manufacturing protective screens, polycrystalline plates are to be cut, grinded and polished, and it turned out that under such procedures some specific problems arise.

First, the plates could crack during their machining. To avoid it, we have developed a method that made it possible to grow plates under conditions of a flat shape of the crystallization front. This method made it possible to increase the mechanical strength of rather thick (15–25 mm) plates, but in the case of large plates of smaller thickness (less than 8–10 mm), the flat crystallization front did not have the same effective impact on the plate strength.

Second, the plates behaved during machining like a material with some porosity which caused the appearance of micro-defects on the surface, that it was necessary to specifically remove.

And, finally, at plate polishing, unpleasant smell was felt, and the production staff could even feel headaches and nausea, if working without personal protective equipment.

We assumed that all these problems arise for the same reason, that is the presence of dissolved hydrogen in germanium. In fact, of all the chemical compounds that hypothetically could be released from the plates, only the compounds with hydrogen are toxic.

This article presents experimental data in support of the assumption of the presence of hydrogen in optical germanium and a method of ultrasonic processing is described for removing dissolved hydrogen from germanium plates which results in a significant improvement in their strength and structure.

2 Related works and considerations

To become clear from which sources hydrogen enters in the plates of optical germanium grown under the inert gas ambient, we recall that the main technological processes of production of the raw materials from which optical germanium is produced, are carried out in the hydrogen flow. Those are the process of obtaining metallic germanium by chemical reduction of germanium oxide and the process of zone purification of the obtained metallic germanium.

The solubility of hydrogen in germanium at high temperatures is quite significant: it is known [9] that molten Ge absorbs hydrogen in an amount of 0.186 ml of hydrogen per 1 g of germanium. In reality, however, the amount of absorbed hydrogen in the melt can be even greater, since, as was shown previously [10], the solubility depends on the conditions at the interface between the hydrogen-containing medium and the liquid metal. As for Ge single crystals grown in a hydrogen ambient, it was shown [2] that the hydrogen content in them is 10^{14}–10^{15} cm^{-3}.

During the growth of Ge:Na plates which is carried out in the neutral (inert) gas ambient, i.e., at the absence of gaseous hydrogen, hydrogen which was dissolved in the raw material, can partially evaporate through a large-area crystallization surface. It leads to the formation of pores, and, as a result, the plates become slightly porous. Similar processes have been observed previously in other materials, for example, in the course of solidification of liquid magnesium in the hydrogen atmosphere. It has been shown [11, 12] that, since the solubility of hydrogen in liquid magnesium is about 1.5 times greater than in solid magnesium, a hydrogen gassing occurs at magnesium solidification, and the metal becomes micro- and macroporous.

The hydrogen-based model under discussion made it possible to explain all specific features appeared while plate machining. The porosity of the plates increases their fragility and can lead to plate cracking during their cutting and grinding, especially in the case of relatively thin plates. That part of the hydrogen that remained in the plates after partial evaporation of hydrogen and can be accumulated in the pores, in the interstitial spaces of the germanium lattice or at the grain boundaries, may participate in formation of toxic chemical compounds with germanium during plate machining. Toxicity of these compounds is very high, for example, the concentration of the germane GeH_4 in the air more than 5 mg per 1 m^3 is fatal to humans, and in 1970 the American Conference of Governmental Industrial Hygienists (ACGIH) set its occupational exposure threshold limit value of at 0.2 ppm for an 8-h time weighted average. Furthermore, the restoration of environmental system after the end of the exposure of those compounds lasts at least 10 years.

Based on the above considerations, we set ourselves the goal of developing a technique for reducing the hydrogen content in optical germanium plates. Note that this problem cannot be solved by an often used method of removing hydrogen from various materials by their high-temperature annealing since, as our experiments showed, with such treatments optical germanium crystals lose their high transparency in the infrared spectral range. As an alternative method, we decided to examine the possibility to use, for this aim, the ultrasonic processing both of the raw material and grown plates.

Previously, the methods of ultrasonic treatment of Ge, Si, and compound semiconductors have been used for some decades as a powerful tool of the defect engineering in these semiconductors [13]. It was also shown that, by means of ultrasonic treatment, it was possible to change the microplastic properties of the near-surface region of dislocation-free silicon and achieve the formation of a hardened near-surface layer but the thickness of this layer was very small (about 100 μm) [14].

3 Experimental results and discussion

3.1 Growth of Ge:Na plates

Na-doped optical germanium plates, up to 330 × 120 × 20 mm^3 in size, were grown by a horizontal directional crystallization [15] in a nitrogen ambient. Advantages of this method are its relative simplicity, the ability to accurately set the size of the crystal by growing it in a graphite container (boat) of required geometry, as well as undoubted economic efficiency. As a starting material, a zone-refined polycrystalline germanium with a purity of no less than 6N was used. The grown plates were coarse-grained with a grain size of 1–10 cm^2. The resistance of the plates was fairly uniform along their length, decreasing from the beginning of the plate to its end by no more than 10–12%, say, from 18 Ohm•cm in the initial part of the plate to 16 Ohm·cm in its end part. The reasons for this higher homogeneity in Ge:Na crystals compared, for example, with Ge crystals doped with V group elements, have been discussed by us previously [6, 7]. Applying specially developed techniques, the crystallization front was maximally close to flat, which, in particular, contributed to a reduction in mechanical stresses in the plates. As a result, the plates thicker than 10–20 mm did not crack during their machining, in contrast to the plates grown with a convex or concave shape of the crystallization front. However, as already mentioned in the introduction, the beneficial effect of the shape of the crystallization front on the strength of the crystals turned out to be much smaller in cases where the thickness of the plates did not exceed 8–10 mm.

3.2 Ultrasonic processing of source material and optical germanium plates

Ultrasonic processing of germanium specimens was performed using an ultrasound oscillator UZG-2-UM which had a maximum output power of 2 kW in a frequency range of 18–22 kHz, and an ultrasonic bath of the UZV-25M type. The design of the generator allowed the possibility of setting the system generator-bath in resonance. Transformation of electric current into mechanical oscillations was carried out using a magnetostrictor PMS-2,5-18. To ensure homogeneity of ultrasonic treatment of plates, the working volume of the ultrasonic bath was filled with distilled water. To avoid chipping of the samples in the process of ultrasonic processing, a plastic shock absorber was installed on the metal working surface of the oscillator. To monitor the power and the presence of resonance in the system, a control sample, partially immersed in water, was placed in the ultrasonic bath, to which the piezoelectric sensor was attached. The control was carried out using an oscilloscope. The power and duration of the ultrasound processing were experimentally selected as follows: the control plates were placed alternately in an ultrasonic bath, and then the output power of the ultrasonic generator was gradually changed from 200 to 1300 W. It turned out that at the power of 200–600 W, any changes in the plate surface were not observed. Starting from a power of 600 W, the formation of small bubbles was observed on the plate surface, and the intensity of the bubble formation gradually increased with an increase in power from 600 to 1000 W. At a power of 1000–1300 W, no further increase in the intensity of the bubble formation was observed. The duration of ultrasonic processing of the plates at different capacities was selected experimentally. After ultrasonic treatment, all samples were etched in a polishing etchants, and their surface was examined using a metallographic microscope and an atomic-force microscope. It was found that, at ultrasound processing with a power of 200–1000 W, no visible changes of the plate surface were observed. When the output power of the generator exceeded 1000 W, an erosion of the plate surface was observed, the intensity of which increased with increasing generator power. Thus, we determined that ultrasonic processing of the plates should be performed in the capacity range 800–900 W. Under these conditions, the control plates were kept in an ultrasound bath for 15 min to 2 h. It was found that within the first 25–30 min, the intensity of the bubble formation on the plate surface was maximal, then gradually decreased and, finally, bubble formation completely ceased after 1 h of treatment. It turned out that, under these conditions, the surface erosion was never observed. Based on the results obtained, we chose the optimal parameters for ultrasonic processing, namely, the output power of the generator (800–900 W), the duration of treatment (about 1 h) and the type of a liquid in an ultrasound bath (distilled water).

In Fig. 1 a photograph of the plate surface during the ultrasonic treatment is presented, on which the bubbles on the plate surface are seen. It is noticeable that the formation of bubbles occurs unevenly over the plate surface. To make it easier to observe the end of the process of bubble formation, we "erased" them periodically, for example, using a brush, but very soon new bubbles appeared on the surface. When the bubbles ceased to appear, the processing was stopped, the plates were taken from the bath and dried in air.

After establishing the optimal regime of ultrasonic treatment, the ultrasonic processing was carried out in a tightly closed bath, from which the gaseous products were exited by means of a special nozzle and passed through a water-filled barber for their chemical neutralization.

Note that, we did not succeed in similar effective removing of the gaseous products from the raw material, i.e., from

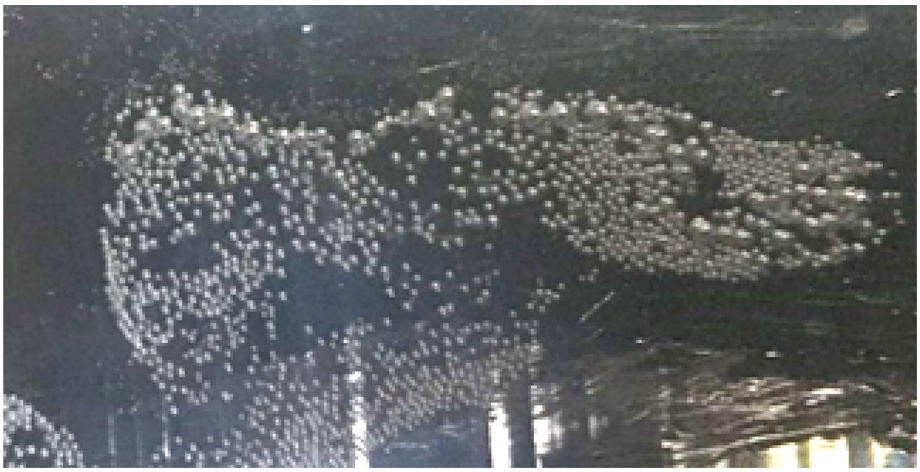

Fig. 1 Photograph of the Ge plate surface section, 30 × 15 mm in area, after 15 min of ultrasonic treatment. The gaseous bubbles are seen on the plate surface

the zone-refined germanium: the quantity of released bubbles turned out to be small, and such processing had practically no effect on the properties of grown plates. We will discuss the possible reasons for this below in the Sect. 3.5.2. For this reason, we refused to process the raw material, and only the grown plates were ultrasonically treated.

3.3 Determination of hydrogen presence in as-grown and ultrasonically treated Ge:Na plates

3.3.1 Measurement of hydrogen content by the method of high-temperature extraction

The hydrogen content in the Ge plates before and after their ultrasonic treatment was determined using the RH-402 analyzer from Leko. The principle of the device operation is based on high-temperature extraction of hydrogen followed by the determination of its amount by means of the highly sensitive thermal conductivity detector. The relative error of such measurements does not exceed 10%, the limit of determination of the hydrogen concentration is about 4.4×10^{14} cm^{-3}.

The measurements showed, that, as a result of ultrasonic treatment, the concentration of hydrogen molecules in the Ge plate decreased from $(1.90 \pm 0.04) \times 10^{17}$ cm^{-3} to $(2.73 \pm 0.20) \times 10^{16}$ cm^{-3}, that is, approximately by 7 times.

3.3.2 Detection of hydrogen by the Raman spectroscopy method

The Raman spectra of the plates were excited by Ar+/Kr+ laser radiation with a wavelength of 488.0 nm and were recorded at room temperature in the inverse scattering geometry using the triple spectrometer Horiba Jobin–Yvon T-64000 equipped with Olympus BX41 confocal microscope. For radiation focusing, a 50× lens with a quantitative aperture of 0.90 was used. When measuring the spectra of Raman scattering, laser radiation was focused on a spot with a diameter of less than 1 μm, and the power of the exciting radiation varied within 0.25–25 mW. The accuracy of determining the frequency of the phonon line was not worse than 0.15 cm^{-1}.

Figure 2a shows the spectra of Raman scattering on optical phonons in Ge polycrystalline plate before (curve 1) and after (curve 2) its ultrasonic processing, measured at room temperature at the wavelength of the exciting laser line 488 nm. In the spectrum of untreated crystals, the lines with maxima at 2930 cm^{-1}, 1612 cm^{-1} and 1445 cm^{-1} were detected. It can be assumed that the first and third of these lines are the Raman signals at 2990 cm^{-1} and 1430 cm^{-1}, which were recorded in Ge crystals treated in a deuterium plasma [2]. The nature of the line at 1612 cm^{-1} is not yet clear to us. Since germanium crystals were not specifically treated with deuterium, it remains to be assumed that the observed lines were associated with deuterium contained in natural hydrogen. It is known that the deuterium content in hydrogen is small (0.011–0.016 atomic %). However, it should be taken into account that the distribution of hydrogen in the crystals studied might be inhomogeneous and hydrogen concentration in some local regions may well exceed the averages. In addition, the radiation of the 488 nm laser line is absorbed in a narrow (approximately 100 nm) near-surface area, where the concentration of hydrogen (and hence of deuterium) exceeds their concentration in the volume. Therefore, it cannot be excluded that the presence of deuterium can indeed be manifested in Raman measurements.

It can be seen from Fig. 2a that after the ultrasonic treatment the discussed lines in the Raman spectrum disappear, which agrees with the assumption of a decrease in the hydrogen concentration and, consequently, in deuterium concentration.

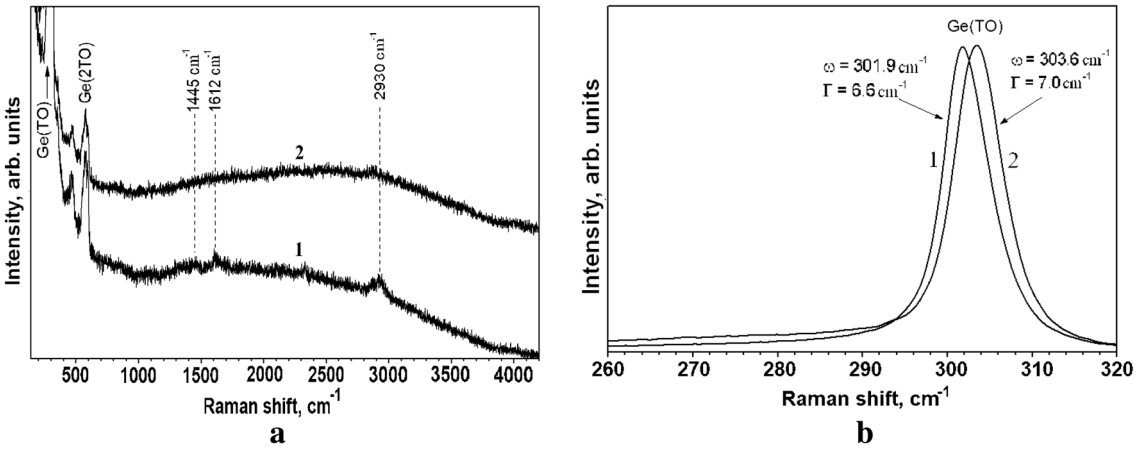

Fig. 2 Room temperature Raman spectra on optical phonons of Ge:Na plate before (curves 1 in **a, b**) and after (curves 2 in **a, b**) its ultrasound processing measured in the range of 100–4200 cm^{-1} (**a**) and 260–320 cm^{-1} (**b**)

We have used such an indirect method of hydrogen detecting since the signal of hydrogen itself in the Raman spectra of Ge is not always manifested, despite the fact that interstitial H_2 is considered to be the dominant hydrogen center in Ge [2]. Only when studied the Ge samples specially treated with pure hydrogen, two sharp lines at 3826 and 3834 cm^{-1} were revealed by Raman measurements at 80 K assigned to orto- and para- H_2 trapped at the interstitial sites of the lattice [1].

3.4 Effect of ultrasonic processing on the formation of macrodefects and optical transmission of optical Ge plates

Before investigating the effect of ultrasonic treatment on the mechanical, structural, and other characteristics of optical germanium plates, it was necessary to verify that such treatment does not impair the especially important parameters of optical germanium, primarily does not lead to the formation of surface macrodefects and does not reduce the optical transmission.

To determine whether the ultrasound treatment leads to formation of macrodefects such as microcracks, micropores, surface microerosion, etc., direct observation of the surface roughness before and after the ultrasonic processing of the plate was made by means of the atomic force microscope (Nano-scope IIIa Dimension 3000) using the silicon probe at a tip radius of 10 nm. The AFM images obtained are shown in Fig. 3. As seen, no macrodefects could be detected on the surface (providing that the plate treatment was performed at optimal parameters indicated above in Sect. 3.2.). Some reductions in the surface roughness observed can be explained by the ultrasonic cleaning of the surface, i.e., by the removal of a minor part of the damaged layer that arose during the mechanical grinding and polishing of the surface.

Figure 4 shows the optical transmission spectra of a flat-parallel polished samples 5 mm thick cut from the large Ge:Na plate. The samples were cut from the plate before (curve 1) and after (curve 2) its ultrasonic processing. The measurements were made at room temperature using Bruker Vertex 70V Infrared Vacuum Fourier Spectrometer. As seen, the ultrasonic processing does not affect the optical transmission of Ge plates in the IR region.

3.5 Effect of ultrasonic processing on mechanical and structural properties of Ge:Na plates

3.5.1 Changes in the Vickers microhardness

Measurements of Vickers microhardness were carried out at a load of 25 g and a holding time under a load of 9 s. Indenter was installed in the central part of the selected crystallite area of at least 10 cm^2 in size, since, as was noted in [16], to increase the accuracy of measurements on polycrystalline materials, it is necessary to conduct measurements on the crystallite of the largest possible area and to install the indenter on as much distance as possible from the crystallite edges.

As measurements showed, the average Vickers microhardness in coarse-grain plates before and after their ultrasonic treatment was 690 kg mm^{-2} and 720 kg mm^{-2}, respectively, i.e., the microhardness increased after this treatment by 4.35%. We note that the maximum Vickers measured on the (111) plane of the Ge single crystal (which is most favorable for these measurements) is 746 kg mm^{-2}, i.e., only 3.5% higher than that measured by us on a crystallite with a randomly chosen crystallographic orientation. This testifies to the fact that, as a result of ultrasonic treatment of polycrystalline plates, the degree of their "looseness" becomes insignificant.

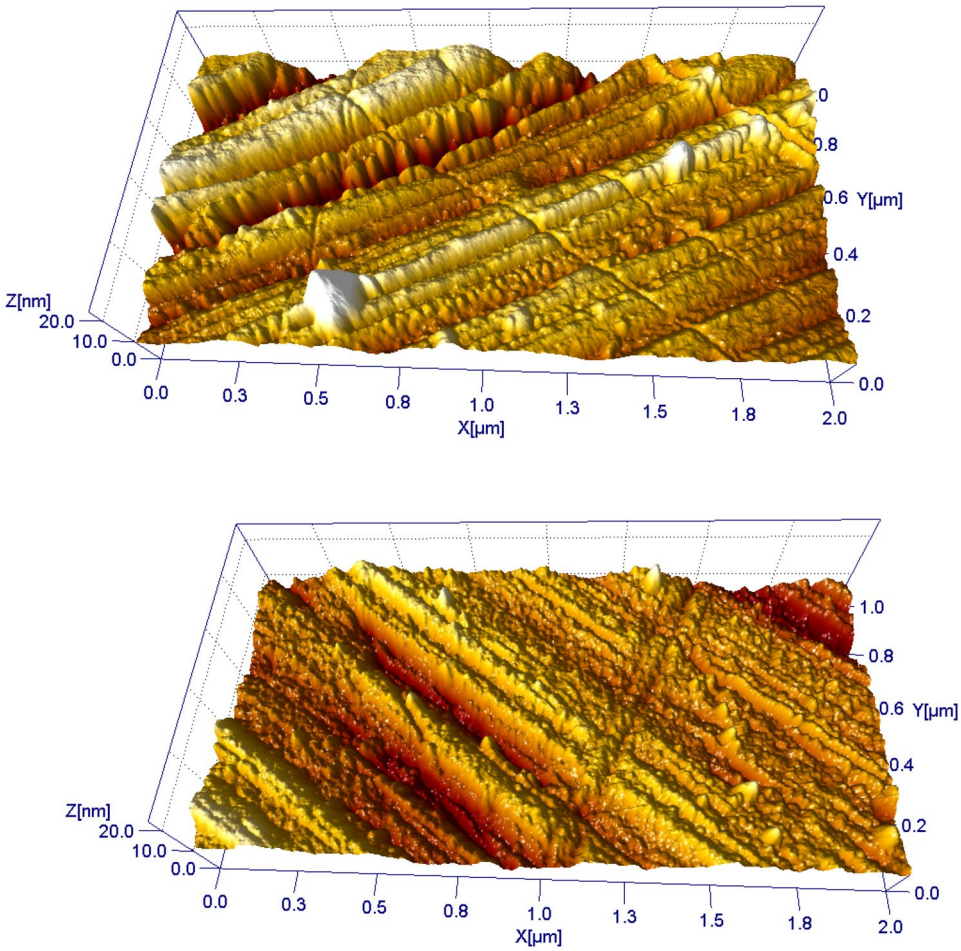

Fig. 3 The AFM images of the Ge:Na plate surface before (top image) and after (bottom image) ultrasonic processing of the plate

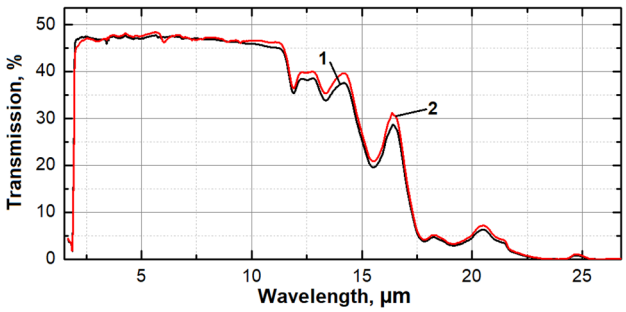

Fig. 4 Optical transmission of polycrystalline germanium samples 5 mm thick cut from the Ge:Na plate before (curve 1) and after (curve 2) its ultrasonic processing. Measurements were carried out at room temperature using the Infrared Vacuum Fourier Spectrometers Bruker Vertex 70 V

3.5.2 Changes in the density, porosity and etch pits density

The evaluation of the change in the plate density resulted from the ultrasonic processing was carried out on a plate in the form of an elongated rectangle with one pointed smaller side. The rectangular part of the plate had a length of 160.00 mm and a width of 116.90 mm. Taking into account the triangular part of the plate, its total length was 196.70 mm. The thickness of the plate was 11.00 mm. Thus, the initial (i.e., before the ultrasonic processing) volume of the plate was 229.34 cm^3.

It was found that after the ultrasonic processing at optimum values of the frequency and power of mechanical vibrations, and also with the optimal treatment time (which was chosen so that the release of gas bubbles from the plates ceased completely), the linear dimensions of the plate were reduced: the length and width of the rectangular part by 0.25 mm and 0.20 mm, respectively, and the total length (taking into account the triangular part)—by 0.30 mm. Thus, the volume of the plate after ultrasonic processing also decreased and became 228.60 cm^3. It should be noted that in view of the fact that the shape of the freely crystallized upper surface of the plate was uneven, it was not possible to accurately measure the change in plate thickness, but since it was relatively small, this should not affect significantly the results of the studies. The weight of the plate after its ultrasonic processing remained unchanged and amounted to 1210.00 g. Hence,

we obtain that, as a result of ultrasonic processing, the volume of the plate decreased by $\Delta V = 0.74$ cm^3, and the density ρ, respectively, increased from the value of 5.276 g cm^{-3} to 5.293 g cm^{-3}, i.e., by $\Delta\rho = 0.017$ g cm^{-3}. According to reference data, the density of Ge single crystals is 5.327 g cm^{-3} at 25 °C, i.e., only by 0.64% exceeds the density of polycrystalline plates processed by ultrasound. It is easy to calculate that in the case of untreated Ge plates, this difference is greater by one and a half times.

The porosity of the untreated plates relative to the treated plates was evaluated by the formula:

$$P = \left(\rho_{tr} - \rho_{untr}\right) / \rho_{tr} = \Delta\rho / \rho_{tr}, \quad (1)$$

where ρ_{untr} and ρ_{tr} are the density of initial (untreated) and ultrasound-treated plates, respectively. It turned out that $P = 0.32\%$.

Let us estimate how this value agrees with the amount of hydrogen in the untreated plates, measured by the high-temperature extraction method (see Sect. 3.3.1). For such estimation, suppose that the pores in such plates are completely filled with hydrogen (which, of course, not necessarily implemented in practice).

The total volume of pores in the plate is 0.32% of 229.34 cm^3, i.e., about 0.73 cm^3. Since the weight of 1 m^3 of hydrogen is 90 g, this volume may be occupied by about 6.5×10^{-5} g or 1.9×10^{19} molecules of hydrogen. Such an amount of hydrogen, located in a plate of 229.34 cm^3 in volume, corresponds to the fact that the concentration of hydrogen atoms in the plate is $1.6 \cdot 10^{17}$ at cm^{-3}. Taking into account the accuracy of measurements of the plate density, evaluative character of calculations made, and also the fact that the complete filling of pores with hydrogen is unlikely, we can assume that this value does not conflict with the concentration of hydrogen in the ultrasound-treated plates 2.73×10^{16} cm^{-3} measured by the high-temperature extraction method.

Note that, at first glance, it may seem that the reduction in porosity and the increase of microhardness resulted from ultrasonic treatment are insignificant and cannot significantly affect the strength of the plates. However, studies of some other types of solids had shown the importance of even small decreases in porosity [17]. In particular, it was revealed that a decrease in the porosity by 3% leads to an increase in the strength of some types of steel up to 20%.

It can be assumed that in the raw material from which germanium crystals are grown, namely in zone-refined germanium, which, in contrast to coarse-grain plates, consists of small grains, the mechanism of hydrogen storage is not the same as in the plates. Most likely, due to other conditions for the solidification of zone-refined germanium, hydrogen is located at numerous grain boundaries and, as indicated above, the ultrasonic treatment used could not release it from this position.

As was indicated above, we observed an intense release of bubbles from the plates during their ultrasonic treatment (Fig. 1). According to our estimations, the diameter of the bubbles ranged from 0.1 to 0.4 mm. Based on the above amount of hydrogen released from the plate, it is easy to estimate that the number of the released bubbles was on the order of several hundred thousand.

Note that, the bubbles were released most intensively from the middle part of the plate along its direction of growth, from which it can be concluded that just this region of plate is most defective. This result agrees with our previous observations [18] that in the plates grown by the horizontal directed crystallization, the mechanical stresses are maximal in the middle region of the plates along the growth direction. Figure 5 shows the distribution of the etch pits density over the surface of the optical germanium plate

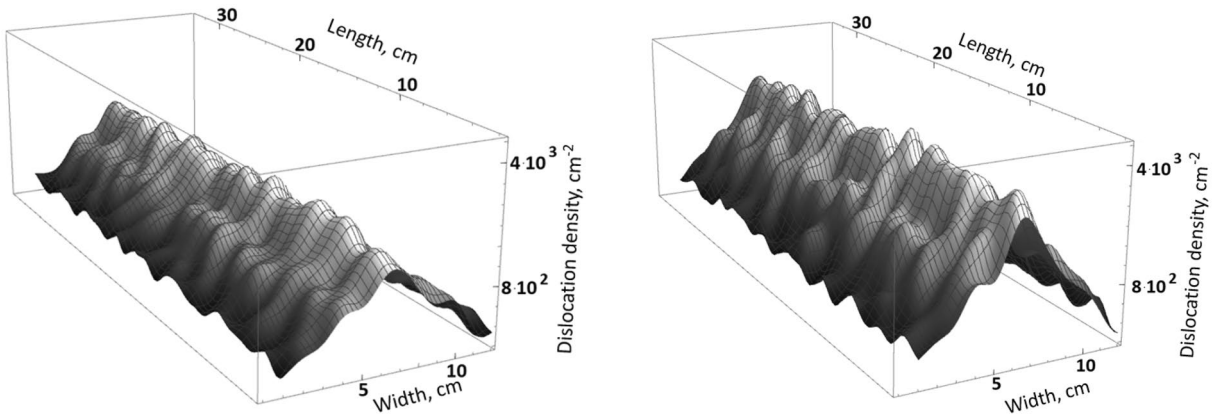

Fig. 5 The dimensional diagrams of distribution of etch pit density over the surface of the same optical germanium plate before (**a**) and after (**b**) its ultrasonic processing. The numbers along the horizontal axes indicate the geometric dimensions of plate in cm, the numbers along the vertical axis—etching pits density in cm^{-2}

330 × 150 × 20 mm in size measured before (a) and after (b) the ultrasonic processing of the plate. The dimensional diagrams were obtained using the automated method for determining the etch pit density [18] as a result of computerized calculations of the etch pits density in 384 points over the surface of the crystal plate. As seen, in both cases, the etch pit density is maximal in the middle region of the plates along the growth direction. The fact that cracking of the as-grown plates during their machining occurs, if at all, just in half along the plate length is consistent with the fact that, as it was shown previously [19], the dislocation density in optical germanium crystals correlates with the value of thermoelastic stress. On the other hand, removing mechanical stress (in our case, by ultrasonic processing) results in the release of energy which leads to dislocation multiplication, provided that the value of this released energy exceeds the energy cost of making dislocations. Just for this reason, the density of dislocations in the middle part of the plate increases after the ultrasonic processing (Fig. 5b) in comparison with the density of dislocations in as-grown plates (Fig. 5a).

3.5.3 Changes in the plate structure revealed from Raman spectroscopy and X-ray diffractometry data

In the Raman spectrum of germanium, the maximum of the TO phonon peak due to the optical vibrations of the Ge–Ge bonds is located at a frequency of approximately 300 cm^{-1} [20]. As our experiments showed (Fig. 2b), as a result of ultrasonic processing of the optical germanium plate, this peak shifted from 301.9 cm^{-1} (before processing) to 303.6 cm^{-1} (after processing) (see curves 1 and 2, respectively). The half-width of the peak remained practically unchanged (6.6 cm^{-1} and 7.0 cm^{-1}, respectively). Note that similar displacement was observed as a result of uniaxial [21] or hydrostatic [22] compression, which caused a decrease in the interatomic distances of the crystal lattice.

Note by the way, that, as it was shown theoretically [23] for the intermetallic alloys, the introduction of hydrogen atoms into the pores of the alloy with a hexagonal structure was accompanied by a significant (by 10–27%) increase in the volume of the crystal lattice, although the lattice type did not change.

The changes in the parameter of the crystal lattice under ultrasonic treatment were also confirmed by X-ray studies. Figure 6 presents X-ray diffraction patterns of the untreated plate (curve 1) and of the same plate after ultrasonic processing (curve 2) measured on the automated X-ray diffractometer HZG-4 with doublet $K_{\alpha 1}$ and $K_{\alpha 2}$ radiation of the Co-anode using a special preset holder of the sample allowing for an independent movement along the ω-axis (coaxial to the 2θ axis of the goniometer) and φ-axis (perpendicular to the surface of the specimen, defines the angle of rotation of the sample around its axis). In the experiment, the axis φ

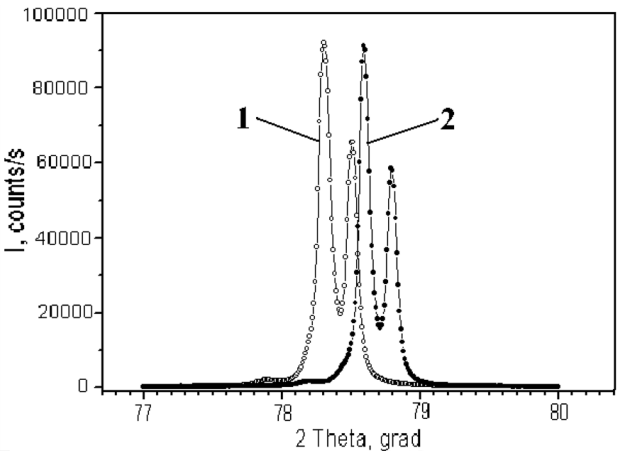

Fig. 6 X-ray diffraction pattern from the Ge:Na sample before (1) an after (2) ultrasonic processing

Table 1 The changes in the parameters of polycrystalline Ge:Na plates resulted from their ultrasonic processing

Parameter	Before ultrasonic processing	After ultrasonic processing
Hydrogen content, cm^{-3}	1.9×10^{17}	2.7×10^{16}
Vickers microhardness, Kg mm^{-2}	690	720
Density, g cm^{-3}	5276	5293
Lattice parameter, Å	5667	5649

was installed perpendicular to the main axis of the goniometer (perpendicular to the ω and 2θ axes).

As it can be obtained from Fig. 6, the ultrasonic processing results in the decrease of the lattice parameter of the Ge:Na plates from 5.667 to 5.649 Å.

Thus, the Raman spectroscopic and X-ray diffractometric data presented above for the untreated and ultrasound-treated plates, are in complete agreement with the observed decrease in the plate volume resulted from their ultrasonic treatment, set forth above in paragraph 3.5.2. The reason for this decrease may be a decrease in the amount (or complete elimination) of hydrogen-containing pores in the crystal lattice of germanium, as well as a decrease in the lattice parameter.

The observed changes in the parameters of polycrystalline Ge:Na plates resulted from their ultrasonic processing are summarized in Table 1.

3.6 Measurements of the fracture toughness and possible causes for increasing the plate strength at ultrasonic processing

As known, an important parameter that determines the ability of a material to perceive the loads acting on them without

forming the cracks, is the fracture toughness. We made an attempt to determine the change in this value resulted from the ultrasonic treatment of the plates. For this aim, an indentation method was used [24].

It is clear that it is impossible to make measurements in the same point of the plate surface before and after ultrasonic treatment since the use of this method is destructive and measurements at the same point before and after ultrasonic treatment are uninformative. On the other hand, the measurements in another area are not meaningful as well, since the initial properties of the first and second areas may be different, for example, because of the different crystallographic orientations of the crystallites.

At the same time, we have managed to obtain an useful and reproducible information as to fracture toughness. It was found that before the ultrasonic treatment, this value equals 0.85 ± 0.01 MPa $m^{½}$ in the middle region of the plate and 0.91 ± 0.02 MPa $m^{½}$ in the peripheral areas of the plate. After the ultrasonic processing, the value of the fracture toughness is leveled over the entire surface and equals about 0.87 ± 0.02 MPa $m^{½}$.

Note that, more recently, a NASA Technical Report have been published [25] in which the fracture toughness was measured both for single-crystalline and large-grain disks of germanium. Among other things, a pessimistic conclusion was drawn that coarse, variable grain germanium is far from being an ideal material for such research. However, by testing different Ge planes by three different methods, the authors concluded that the fracture toughness equaled about 0.68 ± 0.02 MPa $m^{½}$ for {100} and {110} and about 0.74 ± 0.02 MPa $m^{½}$ for{111} germanium planes. Thus, the values measured by us are close to the last results given in the literature, and numerically slightly exceed them.

The alignment of the fracture toughness over the plate surface resulted from the ultrasonic treatment, permits us to make assumptions about the observed increase in the cracking resistance of the plates. As known, for statistical analysis of the strength of brittle materials and for evaluating the probability of their destruction, Weibull model is the most widely used [26]. This model, based on the concept of a "weak link", considers the structure of the material as a chain whose strength is determined by the least strong link in the chain. In the framework of this model, the strength of the plate as a whole should be increased if all sections of the plate have the same strength parameters which exceed (even slightly) the smallest values that were observed at uneven strength distribution.

4 Conclusions

1. With the use of methods of high-temperature hydrogen extraction and Raman spectroscopy, it is shown that the large optical germanium plates Ge:Na grown by horizontal directional crystallization in nitrogen ambient, contain uncontrolled hydrogen. It results in the porosity of as-grown germanium plates (most likely, due to partial evaporation of hydrogen from germanium plates during their crystallization) at a degree of porosity about 0.32%, possible formation of microcracks and surface micropores, frequent cracking of plates of a small thickness, the release of toxic gaseous products during plate machining. All these processes have a negative impact on manufacturing the protective Ge screens for thermal imaging systems.
2. A technique for removing dissolved hydrogen from Ge:Na plates by their ultrasonic processing has been developed. Using the various experimental methods, the effectiveness of such removal has been quantified. It is shown that, under the optimal mode of ultrasonic processing, (1) the amount of dissolved hydrogen in the plates decreases approximately by seven times, (2) in Raman scattering spectra, the optical phonon lines associated with the presence of dissolved hydrogenб disappear, (3) the density of the plates increases, which is confirmed by direct measurements of the density as well as by the shift of the Raman scattering phonon lines due to the optical vibrations of Ge–Ge bonds, (4) the Vickers microhardness increases, (5) the porosity of the plates decreases, and (6) the crystal lattice parameter decreases.
3. It is shown that, as a result of ultrasonic processing, the initial non-uniform distribution of the fracture toughness over the germanium plate surface becomes uniform which, according to the Weibull model of a "weak link", may be responsible for the observed increase in the cracking resistance of the coarse-grain Ge:Na plates.
4. The effectiveness of the ultrasound processing technique developed for the removal of dissolved hydrogen from Ge:Na plates has been confirmed during the industrial manufacture of protective screens for the thermal imaging systems. It was established that, while machining the ultrasound-treated optical germanium plates, they did not crack, the porosity of the plates did not manifested, and also no toxic gaseous products were detected. The latter improved the working conditions of production personnel and ensured environmental safety of industrial production of protective screens.

Acknowledgements This work was funded by the National Academy of Sciences as well as by the Ministry of Education and Science of Ukraine via the Project DZ/35-2017. The authors are very grateful to Academician M. Valakh and Academician Yu. Milman for valuable discussions, Prof. V. Strelchuk and Dr. A. Nikolenko for measuring the Raman spectra, Dr. P. Lytvin for atomic-force microscopic measurements, Dr. I. Goncharenko for measuring the fracture toughness.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

References

1. M. Hiller, E.V. Lavrov, J. Weber, B. Hourahine, R. Jones, P.R. Briddon, Phys. Rev. B **72**, 153201–153201 (2005)
2. J. Weber, M. Hiller, E.V. Lavrov, Mater. Sci. Semicond. Process. **9**, 564 (2006). (https://doi.org/10.1016/j.mssp.2006.08.007)
3. W.L. Hansen, E.E. Haller, P.N. Luke, IEEE Trans. Nucl. Sci. **29**, 738 (1982). (https://doi.org/10.1109/TNS.1982.4335948)
4. V.P. Kalinushkin, V.V. Voronkov, G.I. Voronkova, V.N. Golovina, B.V. Zubov, T.M. Murina, A.M. Prokhorov, in Physical Processes in Laser-Materials Interactions, ed. by M. Bertolotti. *Proc. of the 1980 NATO Advanced Study Institutes Series*, (Springer Science & Business Media, Berlin, 2013), p. 405
5. I.A. Kaplunov, A.I. Kolesnikov, Surf. Investig. X-Ray Synchrotron Neutron Tech. **2**, 14 (2002) (**in Russian**)
6. G.S. Pekar, A.F. Singaevsky, Appl. Phys. A **108**, 657 (2012). https://doi.org/10.1007/s00339-012-6947-x
7. G.S. Pekar, A.F. Singaevsky, Patent of Ukraine for Invention No. 81729, 25.01.2008
8. G.S. Pekar, A.F. Singaevsky, Mater. Sci. Semicond. Process. **64**, 10 (2017). https://doi.org/10.1016/j.mssp.2017.02.026
9. K.A. Bolshakova. Chemistry and technology of rare and scattered elements (Vischaya shkola, Moscow, 1976) (**in Russian**)
10. N. Alba-Baena, D. Eskin, in Light Metals 2013, ed. by B. Sadler. *TMS* (The Minerals, Metals & Materials Society, Pittsburgh, 2013), p. 957
11. P. Röntgen, H. Winterhagen, Aluminium-Arch. **9**, 6–17 (1938)
12. G.V. Raynor. The physical metallurgy of magnesium and its alloys (Pergamon Press, London, 1959)
13. S.S. Ostapenko, N.E. Korsunskaya, M.K. Sheinkman, Solid State Phenom. **65–86**, 317 (2002)
14. I.V. Ostrovskii, L.P. Steblenko, A.B. Nadtochii, Semiconductors **34**, 251 (2000) https://doi.org/10.1134/1.1187989
15. S. Kh, Bagdasarov, *High-temperature crystallization from melt* (Fizmatlit, Moscow, 2004) (in Russian)
16. N.A. Goryunova, A.S. Borshcevsky, L.N. Tretiakov, *Semiconductors and Semimetals, vol. 4, Physics of III–V Compounds* (Academic Press, London, 1968),p. 510
17. M. Balshin, S. Kiparisov, *Fundamentals of Powder Metallurgy* (Metallurgy, Moscow, 1978), p. 184
18. G.S. Pekar, A.A. Singaevsky, A.F. Singaevsky, Semicond. Phys. Quantum Electr. Optoelectronics **19**, 23 (2016). https://doi.org/10.15407/spqeo19.01.023
19. I.A. Kaplunov, Inorg. Mater. **42**, 586 (2006)
20. V.A. Volodin, M.D. Efremov, A.S. Deryabin, L.V. Sokolov, Semiconductors **40**, 1314 (2006)
21. R.T. Payne, Phys. Rev. Lett. **13**, 53 (1964)
22. N.V. Zavaritsky, Lett. JETP **12**, 26 (1970)
23. O.P. Matveeva, Dual Technol. **1** (50), 32 (2010) (**in Russian**)
24. A.G. Evans, E.A. Charles, J. Am. Cer. Soc. **59**, 371 (1976)
25. J. Salem, R. Rogers, E. Baker. NASA Technical Report, 2016. https://instr.nasa.gov//search.jsp?R=20160012342 2018-06-14TO8:12:14 + 00:00Z (2016)
26. W. Weibull, J. Appl. Mech. **18**, 293 (1951)