Semiconductor Physics, Quantum Electronics & Optoelectronics, 2025. V. 28, No 2. P. 194-200.

Optics

Restoration of damaged germanium optical elements of infrared devices

G.P. Malanych*, G.S. Pekar, O.F. Synhaivs'kyi, V.M. Tomashyk, M.M. Lokshyn

V. Lashkaryov Institute of Semiconductor Physics, National Academy of Sciences of Ukraine,
41 Nauky Ave., 03028 Kyiv, Ukraine
**Corresponding author e-mail: galya.malanich@gmail.com*

Abstract. The paper presents the results of research on the restoration of germanium optical elements that have lost their transparency due to operation in extreme conditions. Typically, these optical elements were processed solely as secondary raw materials. The developed cleaning methods allow removing residues of anti-reflective coating to the level of uncontrolled impurities, *i.e.* eliminating their effect on the optical properties of germanium. Experimental evidence shows that the developed cleaning method enables the complete restoration of the parameters of these optical elements.

Keywords: optical germanium, polycrystals, single crystals, thermal imaging technology, restoration of infrared elements.

https://doi.org/10.15407/spqeo28.02.194
PACS 07.57.Kp, 42.70.Km, 42.79.-e, 42.79.Wc, 78.66.Db

Manuscript received 15.04.25; revised version received 05.05.25; accepted for publication 11.06.25; published online 26.06.25.

1. Introduction

Optical germanium crystals are a material commonly used to manufacture passive optical elements of thermal infrared imaging devices for detection, targeting, and guidance systems of armored and aviation equipment [1–7]. These optical elements have good optical properties, but during operation, especially under extreme conditions, they can lose optical transparency, which is a consequence of the degradation of anti-reflective coatings made of zinc sulfide or zinc selenide. Optical elements that have lost their transparency have always been used as secondary raw materials for the purification and growth of optical germanium crystals [8, 9]. It has been determined that the remnants of anti-reflective coating in damaged optical elements, which have lost their transparency, are electrically neutral and transform into electrically active acceptor impurities when anti-reflective coatings are reapplied.

The paper presents the results of the development of a technology for restoring germanium optical elements that have not been mechanically damaged but have lost transparency during operation. The etchant compositions were developed, optimal parameters of chemical and technological processes for removing the anti-reflective coating from the surface and near-surface layer of optical elements were determined, and a method for assessing the efficiency of the degree of chemical cleaning was developed. The obtained results were used to prepare restored optical elements.

2. Research methods and results

The germanium optical elements that had lost their transparency (Fig. 1) were subjected to incoming inspection and preliminary cleaning from foreign contaminants. Mechanically undamaged optical elements were selected for experiments. To develop the technology, fragments of destroyed optical elements with a volume close to 0.5 cm^3 and an anti-reflective coating were also used.

Metal dust and fragments of device frames were removed from the selected optical elements (hereinafter referred to as the material) using a magnetic trap based on a powerful neodymium magnet. After that, the material was ultrasonically treated in a cuvette with ethylene glycol for 40 min. The ultrasonic bath was powered by a 1.2 kW generator UZG-2-4 at a frequency of 24 kHz. As a result of this treatment, adhesive residues and other organic contaminants were removed from the material surface. Then, the material was washed in distilled water and air-dried. To remove the anti-reflective coating, the material was etched at 100 °C in the following chromium mixture: 30 g $K_2Cr_2O_7$ + 900 mL H_2SO_4 + 50 ml H_2O [10]. The etching was carried out until the anti-reflective coating was no longer observed visually. Then, selective control of several fragments was carried out by measuring specific electrical resistivity using the two-probe method and assessing the type of electrical conductivity using the thermo-EMF method [11]. It became clear that all the fragments had *n*-type electrical conductivity and

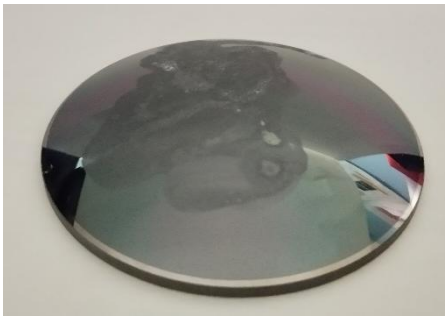


Fig. 1. The appearance of a germanium lens that has lost transparency during operation.

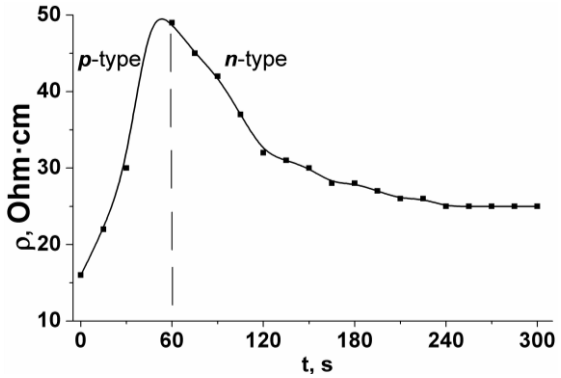


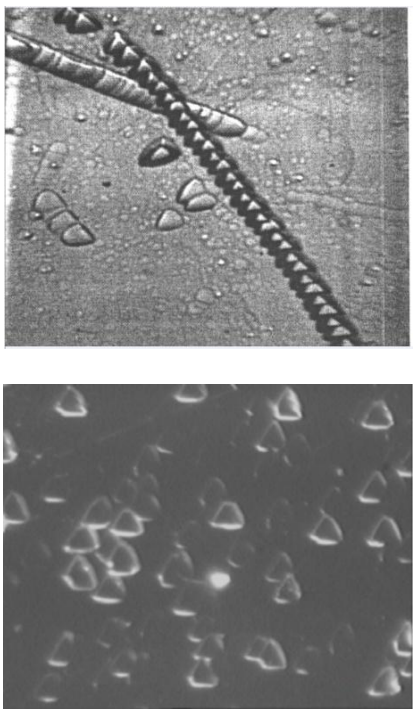
Fig. 2. Dependence of the electrical resistivity on the duration of chemical treatment of control samples in a solution based on hydrochloric acid.

electrical resistivity within the range of 5 to 25 Ohm·cm, which is fully consistent with the standards for optical germanium [12].

Several samples of the etched material were recrystallized at 980 °C in an inert environment using an induction furnace equipped with the STANELCO generator and then cooled to room temperature. The specific electrical resistivity of the recrystallized samples was measured with assessing the conductivity type. It was ascertained that the electrical resistivity of the recrystallized samples was within the range of 0.01 to 6 Ohm·cm, and the electrical conductivity of all samples was the *p*-type. This can be explained by the following. The material of the anti-reflective coating is not completely removed and becomes electrically active. Subsequently, recrystallization of the samples and measurement of electrical resistivity were performed to assess the remaining anti-reflective coating material after etching. The obtained data allowed us to determine the optimal processing time and etchant composition for restoring damaged optical germanium elements, in particular lenses, before re-applying the anti-reflective coating.

A series of experiments were carried out to remove remnants of anti-reflective coatings using known etchants based on hydrochloric and hydrofluoric acids [13]. The dissolution was carried out in a cuvette filled with an etching mixture H_2O_2 + HCl + H_2O with a volume ratio of 1:1:4 [13] for 5 min at 100 °C, then the optical elements were washed in distilled water and dried in a centrifuge. The thickness of the removed germanium layer with the specified etchant was ~ 150 μm. After recrystallization and the electrical resistivity measuring, it was found that this treatment reduces the concentration of surface acceptor impurities to the level of $(2…7)\times10^{14}$ cm^{-3}. Increasing the treatment duration led to excessive dissolution of germanium and did not significantly reduce the content of acceptor impurities (Fig. 2).

Since the used etchant has a selective effect, its use for more than 5 min led to excessive etching of germanium and the formation of a pronounced relief on its surface. Figs 3a and 3b show micrographs of the surface of the etched samples after chemical treatment.



(a) (b)

Fig. 3. Morphology of the Ge surface after chemical dissolution in the 1 H_2O_2 + 1 HCl + 4 H_2O etchant: (a) etching time up to 5 min, (b) etching time 6 min (T = 100 °C); magnification 300×.

If the dissolution occurred in less than 5 min, single pyramidal etching pits were visible on the germanium surface (Fig. 3a). When the dissolution time increased beyond 5 min, the surface began to be etched (Fig. 3b).

Thus, the hydrochloric acid-based etchant does not allow removing the anti-reflective coating from the surface layer of germanium optical elements to the required residual concentration ($\leq 5\cdot10^{13}$ cm^{-3}).

Another disadvantage of this etchant is that it is very aggressive and characterized by a high dissolution rate, and its components are highly toxic. This causes certain difficulties in the preparation and control of the etchant composition and requires the use of specialized

equipment. Similar results were ascertained using hydrofluoric acid-based etchant.

Using the ammonia aqueous solution with hydrogen peroxide, in a molar ratio of NH_4OH/H_2O_2 from 2:1 to 6:1, given in [14], also did not achieve the required surface purity. Additionally, the etching rate of ZnSe is very low (0.2 μm·min^{-1}), which also limits the use of this etchant.

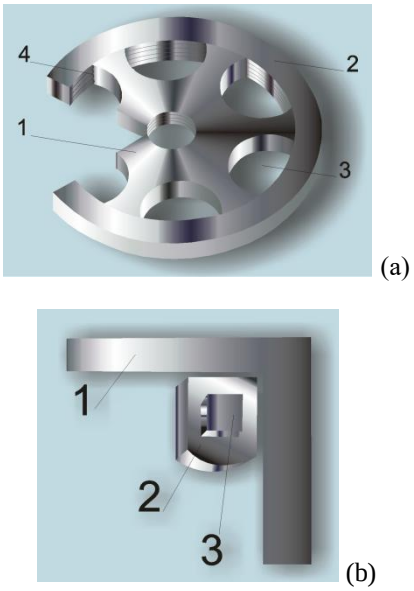
Thus, the above-mentioned etchants are unsuitable for deep cleaning of optical element surfaces, since they strongly etch the surface, making it impossible to reuse, and even with prolonged etching, they do not allow for reducing the concentration of impurities (remnants of the anti-reflective coating) below 10^{14} cm^{-3}.

To eliminate these shortcomings, we have proposed and tested a fundamentally new composition of etchants based on hydrobromic acid, namely H_2O_2 + HBr + H_2O and H_2O_2 + HBr + $C_3H_6O_3$ (lactic acid).

At 100 °C, it is difficult to control the composition of the etching solution and the ratio of its components, so the study was performed at room temperature. Knowledge of the kinetic regularities, mechanism, and nature of the semiconductor dissolution process is an important condition and criterion for selecting appropriate compositions of etchant solutions for polishing as well as anisotropic or selective chemical etching [13]. To study the mechanism of semiconductor dissolution, we used the rotating disk technique and a suitable device for its practical implementation, which is a chemical-dynamic polishing (CDP) unit [15].

To determine the etching rate, the ZnSe samples were fixed onto quartz substrates using piceine. The thickness of the substrates was chosen so that the surface of the crystal to be dissolved and the surface of the fluoroplastic holder were in the same plane. To avoid edge turbulent flows, the substrates were held in the concavity by an outer ring with a width of 8 to 12 mm (Fig. 4a). The difference in thickness of the test sample before and after etching was determined as the arithmetic mean of three or four measurements taken at the same points samples. To ensure that measurements were taken at the same points on the surface, a special template was installed on the measuring table (Fig. 4b). The etching rate was determined using the decrease in the thickness of the sample before and after CDP per unit time (μm·min^{-1}) by applying an electronic indicator TESA DIGICO 400 with an accuracy of ± 0.2 μm. The error of the measured thickness did not exceed 5%. The surface morphology of the ZnSe anti-reflective coating after chemical treatment was evaluated using electron microscopy.

The study was carried out within the following solution concentrations range expressed in vol. %: 12…14 H_2O_2 + 65…70 HBr + 15…25 H_2O (T = 25 °C, the disk rotation rate γ = 86 min^{-1}). In these etchants, the dissolution rate of ZnSe varies within 15.0…25.0 μm·min^{-1}, and the etchants were selective. Solutions within the concentration range: 9…12 H_2O_2 + 25…32 HBr + 55…65 H_2O (T = 25 °C, γ = 86 min^{-1}) have non-polishing properties, and the ZnSe surface is passivated (a brown film was formed). The dissolution rate of ZnSe varies within 10…15 μm·min^{-1}. At the ratios 14…16 H_2O_2 + 65…85 HBr + 5…20 H_2O, the etching rate was 20…25 μm·min^{-1}, and a polished ZnSe surface with a characteristic shine was formed.



(a) (b)

Fig. 4. Fluoroplastic disk for fixing the sample (a): *1* – stand, *2* – outer ring, *3* – hollow for the sample, *4* – stand connection with outer ring, and (b) template for the plates thickness measurement: *1* – template, *2* – glass substrate, *3* – investigated single crystal.

With increasing the processing temperature to 100 °C, the dissolution rate increases significantly, making controlling the composition of H_2O_2 + HBr + H_2O etching solutions practically impossible. Therefore, the removal and evaporation of volatile components occur, which in turn can lead to a shift in the range of unpolished etchants, because the effect of the etching mixtures H_2O_2 + HBr + $C_3H_6O_3$ on the ZnSe surface was investigated.

During treatment of the ZnSe surface with H_2O_2 + HBr + C_3H_6O solutions, the composition with polishing and selective effects were found, and the etching rates were 7…20 μm·min^{-1} (T = 20 °C and γ = 86 min^{-1}). Thus, the solutions H_2O_2 + HBr + $C_3H_6O_3$ are effective in removing the anti-reflective ZnSe coating from the surface of optical germanium at 100 °C.

Based on the mentioned above, we have optimized the composition of the etchant. The criteria for evaluating the effectiveness of the developed etchant were the removal of residual anti-reflective coating to the level of ≤ 5·10^{13} cm^{-3} and minimal germanium dissolution.

Fig. 5 shows a micrograph of the germanium surface after treatment with the bromine-evolving etchant H_2O_2 + HBr + $C_3H_6O_3$ of the optimized composition. One can see that the surface of germanium has no critical damage and is smoother than obtained using etching agents based on hydrochloric and hydrofluoric acids (Fig. 3).

Table. Technological scheme of optical germanium lens restoration.

The view of a lens that has lost its transparency is shown in Fig. 1.

↓

Lens processing in a magnetic catcher
(cleaning the surface from metal contaminants)

↓

Rinsing the lens in an ultrasonic bath and drying
Rinsing with ethylene glycol and subsequent rinsing in distilled water (cleaning the surface from organic contaminants). Drying with air flow (obtaining a dry surface)

↓

Dissolving the anti-reflective coating in the chrome mixture
Etching compositions are based on the solutions of $K_2Cr_2O_7 + H_2SO_4 + H_2O$

↓

Interoperation rinsing and drying
Ultrasonic cleaning of the surface from etchant residues and products of their interaction with the anti-reflective coating. Drying with the air flow (obtaining a dry surface)

↓

Removing anti-reflective coating remnants in a hydrobromic acid-based etching solution
Etchant compositions are based on $H_2O_2 + HBr + C_3H_6O_3$ solutions

↓

Cleaning and washing the lens surface
Ultrasonic cleaning of the surface from etchant remnants and products of their interaction with the anti-reflective coating. Drying with the air flow (obtaining a dry surface)

↓

Soft polishing of lens surfaces up to surface roughness R_z = 50 nm

↓

Cleaning and washing the lens surface
Ultrasonic cleaning of the surface in distilled water. Drying with an air stream
(dry surface)

↓

Applying an anti-reflective coating to the lens surface

↓

The view of the restored lens

Fig. 6 shows the dependence of the electrical resistivity of the recrystallized samples on the duration of etching in the solution $H_2O_2 + HBr + C_3H_6O_3$ with indicating the type of conductivity.

The obtained results show that after the proposed treatment the following effects occur:

1) The remainder of the anti-reflective coating in the volume of germanium crystals are an acceptor impurity with a concentration equal to $5 \cdot 10^{13}$ cm^{-3}.

2) Removal of the anti-reflective material from the surface and from the subsurface layer occurs within 5 minutes at each stage.

3) The thickness of the removed germanium layer is ~ 100 μm.

4) After treatment with a hydrobromic acid etchant, a smooth surface relief is formed.

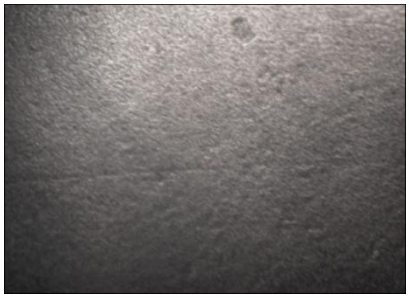


Fig. 5. Morphology of the Ge surface after chemical dissolution in the etchant of optimized hydrobromic acid-based composition (etching time 6 min, magnification 300×).

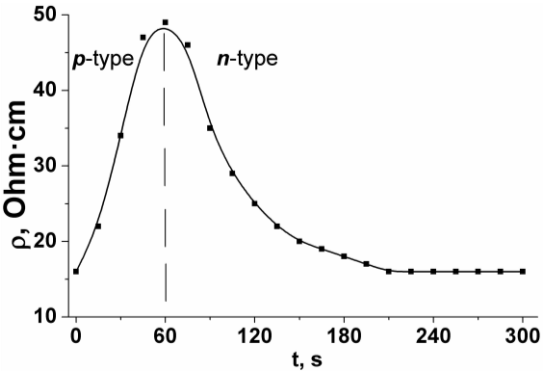


Fig. 6. Dependence of the electrical resistivity of control samples on the duration of chemical treatment in the bromine-releasing etching solution H_2O_2 + HBr + $C_3H_6O_3$.

The germanium optical elements purified from the anti-reflective coating using the developed method were used for the re-application of new anti-reflective coatings with subsequent use in infrared devices.

The technological scheme of optical germanium lens recovery is shown in Table.

3. Discussion of the main research results

When manufacturing anti-reflective coatings on the polished surface of optical germanium parts, the coating material can penetrate the near-surface damaged layer up to 100 μm thick, as well as diffuse depth into the germanium crystals along dislocations, microcracks, and micropores. This material can remain in an electrically inactive state until germanium optical elements and the remnants of coatings are heated to temperatures above 350 °C.

It was not possible to determine accurately the mechanism of incorporation of the remnants of the anti-reflective coating into the Ge crystalline lattice due to their very low concentration. There are methods for direct measurement of such concentrations, namely neutron activation analysis and glow discharge spectroscopy [1], but these methods, even using calibrated standards, do not allow measuring concentrations at the detection limit and with significant error.

Therefore, to determine the impurity concentrations, we used the fact that for germanium, there is a unique relationship between the impurity concentration and the electrical resistivity [16]. Based on the obtained results (Figs. 2 and 6), it can be assumed that the heating to temperatures above 350 °C or recrystallization cause the incorporation of remnants of the anti-reflective coating, into the Ge crystalline lattice and formation of an electrically active acceptor impurity with concentrations above $(5…7)\times10^{14}$ cm^{-3}. This makes germanium opaque within the infrared range. The results of etching damaged optical elements in etchants based on hydrochloric and hydrofluoric acids show (Figs. 2 and 3) that it is impossible to achieve the required level of removal of anti-reflective coating. Therefore, the damaged optical elements can be used exclusively as a secondary raw material for recycling.

Based on the results presented in Fig. 6, we can conclude that we have developed a hydrobromic acid-based etchant and ascertained the etching modes that allow removing remnants of anti-reflective coating to concentrations $\leq 5\times10^{13}$ cm^{-3} without significant damage to the surface of the optical element (Fig. 5).

The advantages of the newly developed hydrobromic acid-based etchants compared to the traditional peroxide solutions with hydrochloric and hydrofluoric acid or ammonium hydroxide are the following:

- effective removal of anti-reflective coating remnants;
- minimal dissolution of the germanium surface;
- avoidance of the use toxic components (Cl_2, NH_3, *etc*.);
- simplification of the process of preparation and use of etching mixtures;
- the ability to control the dissolution rate of the semiconductor by introducing different amounts of organic solvent;
- the ability to control the removal of thin layers from germanium surfaces in a controlled manner;
- no need for complex technological equipment.

The obtained results indicate that after cleaning damaged Ge optical elements, it is possible to completely restore optical elements that have lost transparency due to degradation of the anti-reflective coating, but were not mechanically damaged.

4. Conclusions

It has been experimentally proven that the developed cleaning technology allows completely restoring the Ge optical elements that have lost their transparency during operation, but have not been mechanically damaged.

The developed cleaning methods allow removing the remnants of the anti-reflective coating to the level of uncontrolled impurities, *i.e*. eliminating their influence on the optical properties of germanium. Additionally, the use of these methods minimally affects the geometric parameters of optical elements and, therefore, the optical parameters of the restored optical elements are identical to the parameters of undamaged ones.

Acknowledgments

This study was supported by the National Research Foundation of Ukraine project #2023.04/0010. The authors are sincerely grateful to all the defenders of Ukraine and emergency workers who made publication of the research results possible.

References

1. Pekar G.S., Singaevsky A.F. Na-doped optical germanium bulk crystals. *Appl. Phys. A.* 2012. **108**, No 3. P. 657–664. https://doi.org/10.1007/s00339-012-6947-x.
2. Pekar G.S., Singaevsky A.F., Lokshin M.M. Sodium-doped germanium crystals as a material for infrared optics and detector technique. *Advances in Microelectronics: Reviews. Book Series.* 2019. **2**. P. 89–125.
3. Ordu M., Basu S.N. Recent progress in germanium-core optical fibers for mid-infrared optics. *Infrared Phys. Technol.* 2020. **111**. P. 103507. https://doi.org/10.1016/j.infrared.2020.103507.
4. Zhao R., Zhao X., Sun S. *et al.* Nonlinear optical characteristics of germanium and its application for generating bound state solitons within Er-doped fiber laser. *Results Phys.* 2023. **51**. P. 106604. https://doi.org/10.1016/j.rinp.2023.106604.
5. Tani K., Okumura T., Oda K., Deura M., Ido T. On-chip optical interconnection using integrated germanium light emitters and photodetectors. *Opt. Express.* 2021. **29**, No. 18. P. 28021–28036. https://doi.org/10.1364/OE.432324.
6. Du H., Wang Y., Li Y. *et al.* Fabrication of the optical lens on single-crystal germanium surfaces using the laser-assisted diamond turning. *Intern. J. Adv. Manufact. Technol.* 2024. **132**, No 9-10. P. 4785–4794. https://doi.org/10.1007/s00170-024-13600-0.
7. Liu Y.-H., Lin C.-P., Chen P.-W. *et al.* Normal-incidence germanium photodetectors integrated with polymer microlenses for optical fiber communication applications. *Sensors.* 2024. **24**, No 13. P. 4221. https://doi.org/10.3390/s24134221.
8. Fretty P. Potential supply issues have optics manufacturers and the U.S. government looking at alternative materials to head off disaster. *Optics Industry Addresses the Germanium Issue.* July 25, 2024. https://www.laserfocusworld.com/optics/article/55127439/lightpath-technologies-inc-optics-industry-addresses-the-germanium-issue.
9. Chen W.-S., Chang B.-C., Shuai C.-K. Improve subsequent leaching efficiency and extraction rate of germanium in optical fibre cables with pre-treatment. *IOP Conf. Series: Mater. Sci. Eng.* 2020. **720**. P. 012005. https://doi.org/10.1088/1757-899X/720/1/012005.
10. Tenne R., Flaisher H. Photoelectrochemical etching of ZnSe and nonuniform charge flow in Schottky barriers. *Phys. Rev. B.* 1984. **29**, No 10. P. 5799–5804. https://doi.org/10.1103/PhysRevB.29.5799.
11. Vorobyov Yu.V., Dobovolsky V.N., Strikha V.I. *Methods for the Study of Semiconductors.* Kyiv: Vyssha Shkola, 1988 (in Ukrainian).
12. TU 48-4-522-89. Crystals of optical germanium. TU 2001-04-09 (in Ukrainian).
13. Walker P., Tarn W.H. *Handbook of Metal Etchants.* CRC Press LLC, 1991.
14. *US Patent № 5,445,706*. Aug. 29, 1995. Wet treatment adapted for mirror etching ZnSe. Y. Okuno, H. Tamura, T. Maruyama.
15. Malanych G.P., Stanetska A.S., Stratiychuk I.B., Tomashyk V.M. Technological scheme of mechanical and chemical plates treatment of PbTe and $Pb_{1-x}Sn_xTe$ solid solutions for obtaining polished surface of single crystal. *Mater. Today: Proc.* 2021. **35**, No 4. P. 558–562. https://doi.org/10.1016/j.matpr.2019.10.055.
16. Bishop P.J., Gibson A.F. Absorption coefficient of germanium at 10.6 μ. *Appl. Optics.* 1973. **12**, No 11. P. 2549–2550. https://doi.org/10.1364/AO.12.002549.

Authors and CV

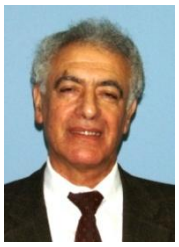
Halyna P. Malanych, PhD, Senior Researcher, Deputy Head at the Department of Chemistry and Technology of Semiconductors, V. Lashkaryov Institute of Semiconductor Physics, of NAS of Ukraine. Field of researches: semiconductor chemistry, chemical treatment of the semiconductor surfaces.
https://orcid.org/0000-0001-7919-8483

Grygoriy S. Pekar, Doctor of Phys. & Math. Sciences, Professor, Head at the Department of Chemistry and Technology of Semiconductors, V. Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine. Field of researches: technology and physics of semiconductor crystals and structures. E-mail: gpekar1@gmail.com,
https://orcid.org/0000-0002-8938-3591

Vasyl M. Tomashyk, Doctor of Chemical Sciences, Professor, Leading Scientific Researcher at the Department of Chemistry and Technology of Semiconductors, V. Lashkaryov Institute for Semiconductor Physics, NAS of Ukraine. Field of researches: semiconductor chemistry, phase equilibria in the semiconductor systems, chemical treatment of the semiconductor surfaces.
E-mail: tomashyk@isp.kiev.ua,
https://orcid.org/0009-0000-0943-5287

Alexandr F Singaevsky, PhD, Senior Reseacher at the Department of Chemistry and Technology of Semiconductors, V. Laskaryov Institute of Semiconductor Physics, NAS of Ukraine. Field of researches: technology and physics of semiconductor crystals and structures

E-mail: 511alexsin@gmail.com,
https://orcid.org/0000-0002-8331-8688



Mykhailo M. Lokshyn, PhD, Senior Researcher at the Department of Chemistry and Technology of Semiconductors, V. Laskaryov Institute of Semiconductor Physics, NAS of Ukraine. Field of researches: technology and physics of semiconductor crystals and structures.

E-mail: lokshinmm@gmail.com,
https://orcid.org/0000-0002-3329-0089

Authors' contributions

Malanych G.P.: conceptualization, methodology, investigation, analyzing the data, validation, writing – original draft, writing – review & editing.
Pekar G.S.: investigation, visualization, resources, formal analysis, writing – review & editing.
Synhaivs'kyi O.F.: methodology, investigation, data curatorship, analyzing the data, validation, writing – original draft, writing – review & editing.
Tomashyk V.M.: conceptualization, methodology, resources, supervision, validation, investigation, project administration, writing – review & editing.
Lokshyn M.M.: visualization, writing – review & editing.

Відновлення пошкоджених германієвих оптичних елементів приладів інфрачервоної техніки

Г.П. Маланич, Г.С. Пекар, О.Ф. Сингаївський, В.М. Томашик, М.М. Локшин

Анотація. У роботі наведено результати досліджень з відновлення германієвих оптичних елементів, які втратили прозорість у результаті експлуатації в екстремальних умовах. Зазвичай такі оптичні елементи підлягали переробці виключно як вторинна сировина. Розроблені методики очистки дозволяють видалити залишки антивідбиваючих покриттів до рівня неконтрольованих домішок, тобто усунути їх вплив на оптичні властивості германію. Експериментально доведено, що розроблена методика очищення дає можливість повністю відновити параметри таких оптичних елементів.

Ключові слова: германій оптичний, полікристали, монокристали, тепловізійна технологія, відновлення інфрачервоних елементів.