Large polycrystalline optical germanium Ge:Na plates with improved optical parameters and their application

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Abstract. It has been experimentally shown that transmission and scattering of IR radiation by Na-doped coarse-grained large germanium plates are the same as of Ge:Na single crystals and exceeds the parameters in the commonly used optical germanium Ge:Sb grown from the same raw material. Being based on experimental results, a conclusion has been made that the nature of the dopant in Ge:Na is a decisive factor defining its optical parameters, along with the usual requirements of high purity of the raw material, resistance values below about 20 Ohm·cm and a sufficiently large grain size (for polycrystalline material). It is assumed that, most likely, Na in Ge:Na, contrary to Sb in Ge:Sb, doesn’t form impurity clouds that scatter the incident IR radiation. The advantages of the polycrystalline Ge:Na as a material for IR optics were proved when using it for industrial manufacturing the protective screens for night vision systems.

Keywords: Na-doped germanium, large coarse-grained plates, optical transmission, protective screens, thermal imaging systems.

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I. Introduction

Optical germanium that is transparent to infrared (IR) radiation in the regions of both atmospheric transparency windows is one of the basic materials for IR optics. For more than half a century, the mono- and polycrystalline optical germanium is used to manufacture lenses, windows, and other passive elements of IR technique. Recently, a special attention has been paid to polycrystalline optical germanium that is cheaper and, what is important, may be more easily grown in the form of large-area plates required, in particular, for production of protective screens for thermal imaging systems of night vision.

To ensure that the replacement of single crystals with polycrystalline material does not impair the parameters of Ge-based devices, it is necessary to know to what extent different characteristics, and primarily the optical parameters, of polycrystalline optical germanium are inferior to the characteristics of single crystals and whether it is possible to make these characteristics as close as possible. The technological and physical experiments described in this paper are aimed at solving this problem. It has been shown that, by using a properly selected doping of optical germanium, namely, doping with an interstitial donor impurity (Na), but not with a commonly used substitutional donor impurity (such as Sb), it is possible to grow large polycrystalline plates, which optical parameters are the same as in the good-quality single crystals of optical germanium grown from the same raw material.

2. Related works

As it was shown about half a century ago [1], to provide a high transparency of Ge crystals in the IR region, doping with donor-type impurities in a definite range of their concentrations has to be used. This doping has to ensure the n-type conductivity of germanium, which makes it possible to avoid, upon absorption of IR radiation, direct transitions of carriers between the sub-bands of the valence band. Just these direct transitions lead to high absorption of IR radiation in Ge. However, the level of Ge doping with donor impurities must be not too high to avoid increased absorption by free electrons.
It was concluded that the density of donors which provides the crystal resistivity from 5 to 40 Ohm-cm (the respective values of free electron concentrations lies approximately between 4·10^{14} and 5·10^{13} cm^{-3} [2]) is optimal for preparing the optical germanium for applications in IR technique. In fact, the best optical parameters were observed experimentally in somewhat narrower resistivity ranges. According to our experiments, this region lies between 10 and 25 Ohm-cm at room temperature, which roughly coincides with some data published previously [3, 4].

The donor impurity that is most often used and provides the necessary optical properties of Ge crystals is antimony, atoms of which substitute Ge atoms in the crystal lattice. However, we have managed to dope Ge crystals with an interstitial Na and to show that the optical parameters of single-crystalline and coarse-grained Ge:Na are better as compared with those of Ge:Sb grown from the same raw material [5, 6].

In recent years, in connection with the requirements of industry to reduce the cost and at the same time to increase the size of optical germanium crystals that can be provided by using an available polycrystalline material, the issues related to the differences in the optical characteristics of single-crystalline and polycrystalline optical germanium have become rather topical [7-13].

A detailed critical comparison of the characteristics of single-crystalline and polycrystalline optical germanium has been carried out by Schroeder and Rosolowski in 2013 [7]. In particular, the well-known fact has been analyzed that, for the wavelength of 10.6 µm, the values of the manufacturer’s guaranteed transmission of the 1-cm-thick single-crystalline and polycrystalline windows are 0.020 and 0.035 cm^{-1}, respectively. It means that the transmission of 10.6-µm radiation by uncoated crystals of both types are 45.86 and 44.99%, respectively, and in the case of using a perfect antireflection coating, transmission equals 98.02 and 96.56%, respectively. Thus, the difference in transmission of the single-crystalline and polycrystalline optical germanium with an antireflection coating exceeds 1.4%. On the assumption of these data, as well as the data on the differences in the index homogeneity, the authors came to the conclusions that (i) the use of Ge single crystals is desirable, if 1% improvement in optical transmittance is crucial, for example, for systems containing multiple Ge lenses in series, and (ii) polycrystalline germanium is more suitable for creation of optical elements with small to medium sizes.

At the same time, some authors had more optimistic view on the use of polycrystalline germanium. In particular, Adams [8] concluded that, since, on the one hand, the polycrystalline blanks may consist of large crystallites and, hence, may have few grain boundaries, but, on the other hand, the single crystals may contain many dislocations, many small angle boundaries and many slip planes, from the viewpoint of optical elements manufacturing, the Ge blanks classification as single-crystalline and polycrystalline is an oversimplification.

The author approves that polycrystalline material in most cases can be used on a par with single crystals, only it must be properly manufactured. In particular, as it was shown by McNatt and Handler [12], polycrystalline germanium should have a sufficiently low resistivity, say from 4 to 25 Ohm-cm. This is necessary in order to compensate acceptors (for example, Cu and Au), which may be accumulated at the grain boundaries, creating regions of increased absorption. Such regions, with resistivity above 40 Ohm-cm, were detected by Lewis et al. [13] in Ge with the resistivity between 20 and 40 Ohm-cm, and the authors have concluded that this effect associated with the grain boundaries can be eliminated by using high-purity starting materials.

Lines 1 and 2 in Table 1 show the values of Ge theoretical maximum transmission and the recommended minimum transmission taken from [8]. The lines 3 to 5 show the experimental values of transmission of Ge:Sb and Ge:Na single crystals grown from the same raw material. Those data were first published by us in [14].

Let’s make two comments to Table 1. Firstly, sometimes the values of Ge transmission at different wavelengths given in the literature are higher than even theoretical values shown in the line 1 of Table 1. Most probably, this is due to the overestimation of the transmission values obtained by those measurements in which scattering and its apparent contribution to the crystal transmission was not taken into account [10]. Secondly, although the values of transmission of Ge:Sb crystals shown in the line 3 are very close to the data given by industrial manufacturers of optical germanium, sometimes they can be slightly larger or smaller for some wavelengths. Most likely, this is due to the different chemical contaminations in the raw materials and proves once again that in order to establish the role of dopant in

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formation of material properties, it is necessary to compare the transmission of differently doped crystals grown in the same laboratory and from the same raw material.

As it was shown by us previously [5], among the advantages of Ge:Na crystals over Ge:Sb crystals there is a significantly lower scattering of transmitted radiation. This is due not only to the fact that introduction of small-size interstitial Na atoms into germanium leads to less distortions of the crystal lattice as compared with substitutional impurity Sb in Ge, but also to lower solubility of Na in Ge (about $10^{13}$ atoms/cm$^3$) [6] as compared with Sb. The maximum solubility of Sb in Ge crystals is $1.2 \times 10^{19}$ atoms/cm$^3$ [15], Sb has a retrograde solubility in Ge, and, as a result, while cooling the grown Ge:Sb crystals from the growth temperature to the room one, second-phase inclusions of Sb with characteristic sizes about 6…9 µm are formed, and they scatter the infrared radiation [16]. Unlike this, the density of dissolved Na in Ge is low, and formation of impurity clouds [17] that serve as scattering centers in Ge:Na is likely much less than in Ge:Sb.

3. Growth of polycrystalline Ge:Na ingots and plates

As a starting material for crystal growing, a zone-refined polycrystalline germanium material with a purity of at least 6N was used. Polycrystalline Ge:Na bulk crystals were grown by two methods.

For manufacturing comparatively small optical germanium windows, polycrystalline Ge:Na ingots were pulled from the melt by Czochralski method in the form of rectangular parallelepipeds $88 \times 82 \times 47$ mm in size. The ingots were grown on single-crystalline seeds inside a graphite shaper which presents an empty box with the above-indicated internal dimensions. Growth was carried out in the argon or helium ambient. Among the advantages of this method [18] are its relative simplicity, the capability to grow very large plates as well as their cost-effectiveness. The grown plates were polycrystalline with the grain sizes of 1 to 10 cm$^2$. Similarly to Ge:Na crystals pulled from the melt [5], 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 by 10-12%, most often approximately from 18 to 16 Ohm-cm. The reasons for this higher homogeneity in Ge:Na crystals as compared, for example, with crystals doped with V group elements, have been discussed by us previously [6]. Using specially developed technological tricks, the crystallization front was made maximally close to flat, which, in particular, contributed to a reduction of mechanical stresses in the plates [18].

4. Results and discussion

4.1. Optical transmission of Na-doped mono- and polycrystalline germanium

In Introduction, it was already noted that in the traditional optical germanium Ge:Sb the absorption coefficient (more precisely, the coefficient of radiation extinction) in mono- and polycrystals differs by more than one and a half times (0.02 and 0.035 cm$^{-1}$, respectively). Before analyzing the properties of mono- and polycrystalline Ge:Na, we shall discuss the difference in the optical transmission of Ge:Na and Ge:Sb single crystals. The doped crystals of both types were grown from the same raw material, as well as by using the same technological equipment and the same growth conditions. Optical transmission of the grown crystals is shown in the lines 3 and 4 of Table 1. The line 5 of Table shows by how many percent the transmission of Ge:Na exceeds the transmission of Ge:Sb. For example, at the practically important wavelength of the incident radiation 10.6 µm, the transmission of Ge:Na is about 1.75% higher than that of Ge:Sb crystals.

However, while using optical germanium plates as a material for fabrication of the protective screens, the value of the radiation scattering is especially important to provide an image of good quality. It is known [10] that in Ge:Sb crystals the radiation scattering may be rather significant and can even reach 23%. Taking into account that the maximal transmission of IR radiation achieved in optical Ge equals 47% (without antireflection coating), this means that up to half of the total radiation passing through the crystal can deviate from its original direction. Previously we determined [5] that the values of the radiation scattering and directional transmission of 10.6 µm radiation equal 4.0-5.0 and 39%, respectively, in Ge:Sb and 1.2-1.5 and 41%, respectively, in Ge:Na. In these experiments, we investigated crystals Ge:Sb and Ge:Na grown by us from the same source material, as well as the industrial crystals Ge:Sb. It turned out that the results obtained for Ge:Sb crystals of both origins were almost identical.

Fig. 1a shows the optical transmission spectra of two randomly selected windows with the diameter 2.54 cm and thickness 0.1 cm, cut from the polycrystalline Ge:Na ingot, $88 \times 82 \times 47$ mm in size, grown by us by pulling from the melt in He atmosphere, as described above in the section 2.1. The measurements were carried out at the “Axsys Technologies” company (USA). For comparison, the transmission of single-crystalline Ge:Sb window used a reference one is shown. It can be seen that the transmission of the reference single-crystalline sample exactly coincides with the transmission of one of the Ge:Na polycrystalline
The above results allow us to draw important conclusions concerning the optical properties of polycrystalline optical germanium Ge:Na. They show that, in addition to previously established such important technological factors as the reduction of the temperature fluctuations in Ge melt, sustaining the instant crystal growth rates and other improvements of the growing conditions [10], the nature of the dopant also can play a decisive role in improvement of optical parameters of the crystalline optical germanium. As the above results show, replacing the substitutional impurity Sb with the interstitial impurity Na not only leads to the improvement of the optical parameters of single crystals without taking special technological efforts, but also the optical characteristics of polycrystalline ingots and polycrystalline large plates, regardless of the method of their growing, are the same as in high-quality single crystals. We emphasize once more that this is most likely due to the absence, in Ge:Na, of impurity clouds, which serve as scattering centers for IR radiation (see above, Section 2).

4.2. Practical benefits of using polycrystalline Ge:Na plates

When manufacturing protective screens based on polycrystalline Ge:Na plates, it turned out that the above advantages of this material are most noticeable at the final stage of screen manufacturing. In particular, it was found that the comparatively small excess of the Ge:Na optical transmission in comparison with Ge:Sb becomes higher by a few percent after applying an anti-reflective coating on both sides of the plate. This is apparently associated with a difference in the nature of the defects that exist at the crystal-coating interface in both types of materials.

From the viewpoint of the practical use of Ge:Na crystals, it is very important that IR radiation scattering in Ge:Na single and polycrystals is lower than in Ge:Sb crystals grown from the same raw material. As it was mentioned above in Section 3, when Sb is replaced by Na as a dopant in Ge, the values of the radiation scattering decrease more than threefold. In the well-known Beer–Lambert–Bouguer law $I(d) = I_0 \exp(-k_\lambda d)$, (where $I_0$ and $I(d)$ are the intensities of the incident and transmitted radiation, $d$ is the sample thickness), the extinction coefficient $k_\lambda$ includes the values of the coefficients that determine the absorption of radiation by the crystal lattice and the scattering of radiation in the sample. Since in the case of replacing Sb by Na, as a rule, the scattering decreases much more strongly than absorption, it could be expected that, when using Ge:Na protective screens in thermal night vision systems, the optical resolution of the image will be noticeably higher than when using Ge:Sb screens.

Figs. 2a and 2b shows the results of testing the thermal imaging system of night vision using the protective screens made of Ge:Sb (a) and Ge:Na (b) polycrystalline plates grown from the same raw material. The tests were carried out at night, the night vision system with a Ge:Na protective screen was brought up to such a maximum distance from the object, at which it was already possible to determine its presence and
nature. At a distance to the monitored object 3580 m and while using a coarse-grained Ge:Na protective screen, the experienced observer confidently determined that the monitored object is seen and it is a truck of the brand “Gazelle” (Fig. 2b). However, after replacing the Ge:Na protective screen with a Ge:Sb protective screen with the same geometric parameters, the existence of the object could be also detected but its nature could not be distinguished (Fig. 2a).

Taking into account that the photos shown in Fig. 2 may seem not very convincing and someone can doubt the observer's conclusions about those images that he saw with his eyes and in order to provide the quantitative information about the quality of both images shown in Fig. 2, we estimated roughly the degree of blurring for those images. Blurring is usually understood as unclear outlines of the elements of the image, which does not allow to discern details of the image. One of the methods for estimating the degree of image blur is based on the value of the Weibull distribution parameter $\eta$: the greater the degree of blur, the closer the value of this parameter approaches the value of 2 [19]. According to this criterion, the image in Fig. 2b does not exceed the value of $\eta = 1.3 \ldots 1.4$ which is considered quite sufficient to establish the nature of the object, while the image in Fig. 2a exceeds the value of $\eta \approx 1.7$.

Owing to rather good optical parameters of large polycrystalline Ge:Na plates as well as to reliability and comparative cheapness of their growing, for several recent years this material has already found successful industrial use to create protective screens with dimensions up to 400 cm$^2$ for thermal imaging systems.

5. Conclusions

It has been experimentally shown that the practically important optical parameters, such as transmission and scattering of IR radiation, of Na-doped coarse-grained large germanium plates is the same as of Ge:Na single crystals and are better than the parameters of the commonly used optical germanium Ge:Sb grown from the same raw material. The best values of those optical parameters of mono- and polycrystalline Ge:Na in comparison with Ge:Sb may be attributed to the absence of impurity clouds in Ge:Na (primarily as a result of the low solubility of Na in Ge) which scatter the incident IR radiation. It is concluded that the nature of the dopant in mono- and polycrystalline optical germanium is a decisive factor determining optical parameters of this material, along with the degree of chemical purity of the raw material. Under conditions that the value of the resistivity in polycrystalline Ge:Na large plates do not exceed approximately 20 Ohm·cm and the size of the grains is sufficiently large, this material is shown to have important advantages when using it as a material for IR optics, in particular, the best image resolution in thermal imaging systems of night vision. It was proved when using this material in industrial applications.

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References


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