Photoelasticity method for study of structural imperfection of ZnGeP₂ crystals

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The stresses, related to rows and accumulations of dislocations were revealed by photoelastic method for ZnGeP₂ crystals, grown by Vertical Bridgman method. A comparison of information from topographs of photoelastic method and X-Ray topography based on Borrmann method was carried out. It was shown that the strongest contrast is observed on boundaries of dislocation rows and regions of relatively perfect crystals. Photoelastic method gives information about defect structure, where X-Ray topography can not be applied because of high density of defects and disorientation of reflection planes. Because of high sensitivity of photoelastic method the images of defects have larger size then in X-Ray topography. That is why in ZnGeP₂ predominately the total contrast from dislocation rows is fixed. However, in low angle boundaries photoelastic images of separate dislocations were revealed. By comparison with results of simulation it was stated that they are created by edge dislocation of slip system {110}, what confirms the data, obtained by Borrmann method.

Thus, photoelastic method can be from one side a simple and express method of analysis of ZnGeP₂ plates cut along the plane of optical isotropy (001), and from other side an analytical method of identification of dislocations and other defects in this material.

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1. Introduction

ZnGeP₂ (ZGP), a ternary semiconductor compound with chalcopyrite structure is used as a high-performance medium for conversion of laser frequency radiation in the middle IR that allows to solve a lot of problems of high-resolution spectroscopy [1]. The potential transparency range of ZGP is from 0.65 to 12 μm. ZGP demonstrates a high nonlinear optical coefficient ($d_{36}=75 \times 10^{-12} \text{m/V}$), rather high damage threshold. It is also possesses adequate birefringence for phase matching, high hardness, high specific thermal conductivity and a weak temperature dependence of the refractive index. The advantages of ZGP are especially evident in design of lasers tunable in a wide range (2.5–8 μm). These lasers are important elements of optical devices and systems with new nontraditional functions having a great applied importance. The possibility of wider application of ZGP in nonlinear optics depends to a large extent on the progress in the growth of ZGP single crystals of high structural and optical quality. In 0.65–2.5 μm optical region ZGP has a high optical absorption, falling on the pumping radiation range (near 2 μm) when the material is applied for optical parametric oscillations. It is believed, that the absorption is related to high concentration of native point defects. The point defects were well studied by American scientists [2,3].

In practice the production of very perfect single crystals of ZGP is limited by some technological difficulties, related with synthesis and growth of this material. Often the grown crystals have structural defects, which can influence on physical properties of ZGP. In this connection a problem of study of structural perfection of ZGP is important from point of view of science and has a very significant practical interest.

Possibilities of X-Ray topography based on Borrmann effect for study of ZGP defects were well demonstrated in [4,5]. Particular interest has a technique, when in Borrmann method rosettes of contrast from all main types of defects in the crystal lattice are recorded, and from them the all characteristics of the defect are determined [5]. The method is the most effective under study of high absorption and relatively perfect crystals (with dislocation density $N_d < 10^5 \text{cm}^{-2}$) to which the ZnGeP₂ can be attributed. The defect structure of presented samples in this paper was decoded by Borrmann method. The disadvantages of this method are the following: big expositions on shooting, reaching several tens of
hours, a usage of photo process, and usage of X-Ray radiation, potentially dangerous for human health. The method allows to provide only limited number images of defects on the most strong X-Ray reflexes with small Miller indexes.

Another method where structural defects produce the images in form of the contrast rosettes is photoelastic method. This is an optical method to study the stresses based on stress-induced birefringence, or so-called piezo-optical effect. In transparent materials the photoelastic method allows to reveal and quantitatively measure the stresses, arising from external defects and internal stresses, which exist in the material in absence of external stress. The studies of Bond and Andrus [7,8] showed that by photoelastic method not only macroscopic stresses can be revealed but microscopic stresses, connected with individual dislocations also.

In optically isotropic crystals, the dislocations with different from zero edge component of Burgers vector gives a pattern of characteristic stresses, having a form of the rosette of contrast. Studying a field of birefringence near edge or mixed dislocation, parallel to observation axis, one can determine the location of slip plane, sign and magnitude of Burgers vector [9]. The method has already demonstrated its high possibilities when studying individual dislocations in Si, GaAs, GaP and other crystals [10]. Under determined conditions polarization–optical images of defects sufficiently surmount their images in X-Ray topography based on Borrmann effect that testifies about high sensitivity of the method [6]. At the same time the photoelastic method demands from a crystal of special type of dislocation structure: presence of lengthy sections of dislocation lines parallel to the direction of observation. Often, for example, in alum, Seignette salt, corundum the images of separate dislocations prohibit and observed contrast in photoelasticity method corresponds to accumulations of dislocations and slip lines [10].

In spite of clearness and simplicity of realization, presence of theory, allowing to carry out a modeling of defects images and to characterize of revealed dislocations the photoelastic method is relatively seldom applied to study the defect structure of semiconductors. Another aspect of photoelasticity method is widely known and used, it is analysis of distribution of macroscopic stresses in transparent materials and with use of models from special transparent rubber in large and nontransparent constructions.

In present paper we attempt to apply the photoelastic method for analysis of structural perfection of ZGP semiconducting material, grown in Harbin Institute of Technology (HIT), PR China. The early data of X-Ray topography based on Borrmann method showed that in these samples there are rectilinear dislocations, so it is possible to wait from them the patterns of birefringence. The transparency of thin ZGP crystals in red region of optical spectrum (0.65 mkm) allows to apply the usual polarization microscopes.

2. Experimental

ZGP starting material for this study was prepared by horizontal two-temperature method from high purity Zn, Ge and red P. ZGP single crystals were grown by seeded Vertical Bridgman method [11]. The seed orientation was [001]. The studied samples were prepared from two single crystal ingots, the first one was early, obtained several years ago and the other one was recently grown. The samples was cut perpendicular to growth axis with thickness 500–900 μm, mechanically polished before optical study and then thinned and etched in Aqua Regia for X-Ray topography.

For optical study we used the microscope MIN-8 with transitional optical system and digital camera «Olympus C-5060 WZ». Technique of X-Ray topography based on Borrmann method was well described in [4]. A comparison of X-Ray topographs with photoelastic ones for the same crystal samples were carried out.

3. Results and discussion

Under analysis of ZGP plates, cut along (001) plane, being a plane of optical isotropy, the photoelastic images presumably from dislocation rows of different nature and dislocation accumulations have been registered as it is shown in Fig. 1(a). Photoelastic rosettes from separate dislocations in low angle boundaries were fixed also as it is shown in inset in Fig. 1(a). Such images can be easily interpreted using existing theory of contrast for photoelastic method [12]. The direct problem of simulation of polarization–optical image of defect by known deformation field and stresses around it is solved unambiguously. The inverse problem, i.e. calculation of stress field from experimental image of defect, in common case may not have single-valued solution. In this case the situation for photoelastic method is similar to situation in TEM (Transmission electron microscopy) and X-Ray topography. That is why in theory of contrast for these three methods a technique of simulation of image is applied. Starting from existing models of displacement field and stresses around defects and common principles of the defect image formation, the formulas for contrast of concrete defects are obtained. Using these formulas the images of defects are built under different conditions of observation. Comparing the atlas of theoretical images with specific experimental image, the type of defect is identified and its qualitative characteristics are determined. Doing the fitting of the theoretical image under experimental one, the quantitative characteristics of defect are obtained in frames of accuracy of method. To reveal the peculiarities and quantitative characteristics of experimental images the digital treatment of optical photographs is carried out [13].

Let us consider a formation of image from edge or mixed dislocation, perpendicular to surface of plate with thickness d. If the stresses in crystal are absent, the intensity of light, passing
through the crossed nicols is equal to zero. Dislocation, creating the field of elastic stress, gives a enlightenment, which intensity is described by expression [12]:

\[ l = l_0 \left\{ \frac{dgGb}{r^2(1-\nu)} \right\} \cos^2\theta \cos^22(\theta-\alpha), \]  

(1)

where \( l_0 \) is intensity of light, incident on the crystal, \( q \) is photoelastic constant of crystal, \( G \) is a shear modulus, \( b \) is the edge component of Burgers vector, \( \nu \) is Poisson ratio, \( r \) and \( \theta \) are polar coordinates (\( \theta \) is angle, counted from the slip plane of dislocation), \( \alpha \) is the angle between slip plane of dislocation and plane of oscillations in one of the nicols. Formula (1) allows to calculate in principle the sizes of experimental rosettes of contrast in photoelastic method, however, it was received for ideal case of single dislocation in infinite isotropic crystal. In reality the sizes of images are determined by many factors: superposition on stress field from considered defect the stresses of all other defects, present in sample, particularities of optical scheme, value of microscope aperture diaphragm, quality of polarizers, quality of crystal surface treatment. That is why on practice, using the photoelastic method the scientists are limited by analysis of shape of images and to compare the power of defects, they compare the sizes of experimental photoelastic rosettes from them. Let us apply this approach for analysis of images in Fig. 1(a).

From formula (1) follows that the calculated image under observation in crossed nicols may be described by lines of equal intensities of birefringence, given by equation:

\[ R = C \times \cos \theta \times \cos(\theta-\alpha), \]  

(2)

where \( R \) and \( \theta \) are polar coordinates of points of line, \( C \) is a value, proportional to tangential stress in coordinate system, turned relatively to slip plane of dislocation on angle \( \alpha \). Eqs. (1) and (2) describe the rosette of light contrast, which depends from angle \( \alpha \) is six- or four-lobes. Black–white «coloration» in experimentally observed rosettes is related to superposition of microstress fields of individual dislocations and macrostresses, being the sum of long-range fields of all other dislocations of the sample. Signs of birefringence in symmetrical relatively to dislocation lobes of rosette are opposite.

Simulating rosette, corresponding experimental patterns from dislocations on Fig. 1(a) is shown in Fig. 1(b). In the same place a position of the polarizer \( P \), analyzer \( A \) and orientation of dislocation are given. The simulating was carried out for case \( \alpha = 0 \) and its result is six lobe rosette. Large lobes are elongated along slip plane of dislocation. All dislocations in row on insert of Fig. 1(a) form the images of similar type. From comparison of Fig. 1(a) and (b) results that dislocations in row have slip plane \( \{1\overline{1}0\} \) and Burgers vector along direction \([1\overline{1}0]\). Therefore, they are edge dislocations of slip system \( \{\overline{1}1\overline{0}\}/(110) \). This is in a good agreement with data of paper [5], where such dislocations were studied by Bornmann method. From the inset in Fig. 1(a) it is seen that row of dislocations is located in direction \( \{1\overline{1}0\} \) approximately, this is so-called vertical row of dislocations, when slip planes in row are parallel to each other. From Fig. 1(a), (Figs. (2)–4) it follow that in studied crystals the dislocation rows of other character predominate, with directions of \(<100>\) type. The dislocations in these rows are located with very high density, so we were unable to resolve images of separate dislocations in them. It should be kept in mind that a high sensitivity of photoelastic method has some negative side. It results in big sizes of photoelastic rosettes, owing to the images of closely located dislocations blend. In auspicious conditions for Bornmann method, diffraction images are smaller and that is why they better resolve and have more details for interpretation.

Photoelastic images for all studied samples (\#1, \#2, \#3, \#4) are shown in Figs. 2(a)–5(a). Corresponding X-Ray topography images are shown in Figs. 2(b)–5(b). The most bright and contrast images were fixed for samples with higher dislocation density (Figs. 1–4).

The plate \#2 had larger thickness then the plate \#1 (900 and 500 \( \mu \)m correspondingly) and as it was shown from X-Ray studies was much defective than the first one. It had larger dislocation density and disorientation block angles. Path difference under interference of ordinary and extra-ordinary rays, and, therefore, formed photoelastic contrast depends on crystal thickness and value of arising stresses around defects. According to these two reasons for plate \#2 more contrasting photoelastic images were fixed.

Figs. 2b–4b are demonstrated X-Ray topographs obtained by Bornmann method for the same crystal samples. As it seen from the X-Ray topographs the dislocations are distributed non-uniformly, there are small sizes regions practically free from dislocations and regions where a high dislocation density gives a disappearance of anomalous propagation of X-Rays because of strong distortions of crystal lattice. In all the samples the dislocation density is maximal in dislocations rows, elongated along directions \([100]\) and \([0\overline{1}0]\). An average dislocation density is \( N_d \approx 6 \times 10^4 \text{ cm}^{-2} \), the dislocations with curved lines, aggregating in more large structures and slip bands. A high dislocation density in sample \#2 gave a macroscopic bend and exit of separate regions from reflecting position. That is why to obtain diffraction image for the all sample shootings of separate regions with independent tuning at Bragg angle were carried out. General topograph of sample \#2 on Fig. 3(b) was obtained from four separate topographs.
A comparison of X-Ray and photoelastic topographs shows their total correlation. Photoelastic topographs well show the dislocation aggregations in \(<100>\) directions, the most strong contrast is observed on boundaries of dislocation rows and regions of relatively perfect crystal.

From comparison of experimental images follows that photo-elastic method allows to obtain information if there is no possibility to use X-Ray topography based on Borrmann method. In regions where the Borrmann effect is absent because of high dislocation density \((N_d > 10^4 \text{ cm}^{-2})\), for example, regions of crossing of the dislocation rows in Figs. 2(b), 3(b) photoelastic method allows to fix the defect images (Figs. 1, 2(a), 3(a)).

On photoelastic topograph, shown in Fig. 4(a) bright rosettes from large inclusions in the sample volume and stresses also related to inclusions and dislocations near the left edge of the sample are seen. The X-Ray topograph in Fig. 4(b) shows that relaxation of stresses occurred around these inclusions and they were a source of big amount of dislocations. It is seen that the X-Ray topograph in Fig. 4(b) does not give the information in region of right low segment, at the same time the defect images (inclusions and rows of dislocations) are well seen in Fig. 4(a).

Study of new ZGP ingot, obtained after modernization of growth process, showed a great improvement of crystal perfection (the decrease of dislocation density down to \(N_d \sim 2 \times 10^2 \text{ cm}^{-2}\), the decrease of density of dislocation rows and absence of big inclusions). Correspondingly, the photoelastic contrast from the stresses, related with defects, began to be practically indistinguishable with use of our experimental setup. Corresponding pair of images is shown in Fig. 5(a) and (b). Under absence of contrast from defects on photoelastic topographs only peculiarities connected with surface relief are seen.

4. Conclusion

Thus, a direct and nondestructive photoelastic method was applied to ZGP crystals to study defects for the first time. It is shown that the method can be applied for ZGP plates cut only along \((001)\) surface and allow to observe a common pattern of distribution of dislocations and inclusions along the all area of plate. Reliability of interpretation of contrast from accumulation of dislocation is checked in present work by comparison with X-Ray topography data.

The analysis is quite easy since in photoelastic method is possible to obtain a continuous series of images under various values of angles between slip dislocation plane and polarization vector of falling plane-polarized light. In X-Ray topography the scientist is limited only by discrete types of images on the most strong reflexes. As disadvantages of photoelastic method one can call that it practically does not reveal the screw dislocations, with the exception of same cases \([14]\) and demands a high quality of surface sample.

The method is simple in realization, rapid test and safe. In future, seemingly, it will be possible more wide usage of photoelastic method for study of different types of defects in ZGP by the contrast of rosettes from individual defects. A high sensitivity of
the method, stipulated big size and high contrast of images allows in principle to obtain all basic features of crystal defects. Studying a stress field near the dislocations it is possible to determine the features of defects. In particular, from the dislocation photoelastic rosette the direction of dislocation line and Burgers vector are determined. Sign and modulus of Burgers vector can be determined with help of optical compensators.

Thus, the photoelastic method can be used in two ways. From one side it can be applied as express method to estimate the quality of ZGP samples. On other side it can be applied as analytical method of stress measurement under use of modeling and special techniques.

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