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STUDY OF DAMAGED LAYER DEPTH IN THERMOELECTRIC MATERIALS BY X-RAY DIFFRACTION INTERFEROMETRY

The results of investigation of the damaged layer depth after machining of the surface of thermoelectric materials with diamond abrasive powders of different size are presented. A refined model of the damaged layer consisting of: a) a relief zone with polycrystalline structure, from which the kinematic scattering as large as (0.2 – 0.5 d, d – abrasive material grain size) is observed; b) a zone of microcracks, packing defects and dislocation ensembles of (3 – 4 d); c) an elastic deformation zone with an area of (4 – 5 d). This elastic deformation zone is quite long, even during the removal of the first two zones the residual stresses in the crystals still remain.

Key words: X-ray interferometer, moire patterns, X-ray topograms, thermoelement, damaged layer.

Introduction

One of the most important development trends of modern thermoelectricity is microminiaturization of thermoelectric modules which is related to essential reduction of the height of legs. To achieve high thermal and electric parameters of modules with a reduced height of legs, it is necessary to assure minimal contact resistance and high adhesion of metal coating on thermoelectric material. Therefore, the formation of silicon wafers with improved properties in a thin subsurface layer is a relevant task. The depth of the damaged surface (the defective layer depth) of semiconductor materials is an important parameter that needs to be controlled in process sizing. The knowledge of the damaged layer depth makes it possible to optimize processing of semiconductor materials and to choose the best of them, which in its turn will increase their yield. During the semiconductor crystal surface machining in the contact zone with the grains of the diamond abrasive material, the destruction of the original perfect structure and the formation of the damaged subsurface layer take place. Depending on the process conditions of processing, elastic and plastic deformations, microcracks, brittle fracture, local heat treatment and even polymorphic transformations may occur in the subsurface layer [1 – 6]. Naturally, the physical and mechanical properties of the damaged layer substantially differ from those of the original crystal. The study of the structure and depth of the damaged layer is usually performed using the X-ray topography, optical and electron microscopy methods.

As a result of the conducted researches, many models of the damaged layer were proposed, which generally could be reduced to the following: the damaged layer consists of a polycrystalline zone, a zone of microcracks and dislocation clusters, a dislocation zone and an elastic deformation area [1, 2]. It is worth noting that in many papers the dimensions of these zones significantly differ and usually depend on the accuracy of the research methods selected by the authors.

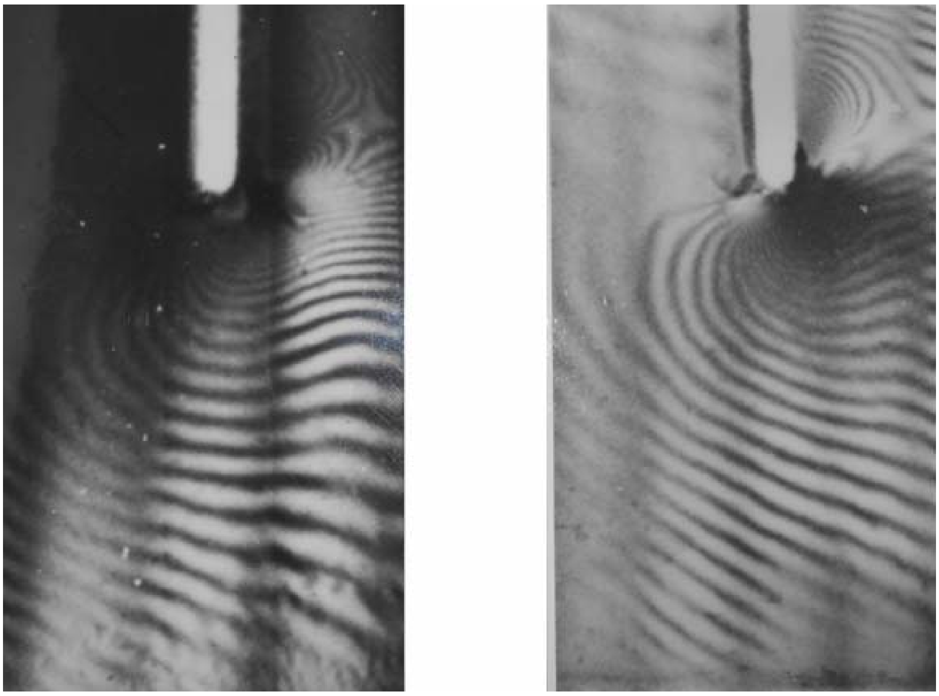
The X-ray diffraction moire (RDM) method, which is highly sensitive to the crystal lattice distortions [7 – 10], can greatly add and expand the information on the structure and level of sophistication of the damaged layer. It can also help to study the homogeneity of *Bi*-*Te* or *Ge*-*Si* based thermoelectric materials with the use of phase moiré topography. Therefore, the study of the damaged layer structure, which occurred during the *Si* surface machining, was conducted in this paper by RDM.

Research methods

The study was conducted on integral LLL-interferometers, made of perfect dislocation-free *Si* single crystals, grown by Czochralski method in the direction [111]. Input surfaces of the interferometers corresponded to crystallographic planes (111). The machining of surfaces of the interferometer analyzer (111), $(\bar{1}10)$, $(11\bar{2})$ was carried out using emery powders M5, M10, M28, and after the abrasive cutting - using an internal cutting edge of the disc. X-ray interferograms and topograms obtained in *CuK*α are radiation ones using reflection $(\bar{2}20)$. The annealing of interferometers was conducted in vacuum 10^{-2} Pa at the temperature of 700 – 1173 K.

Research results

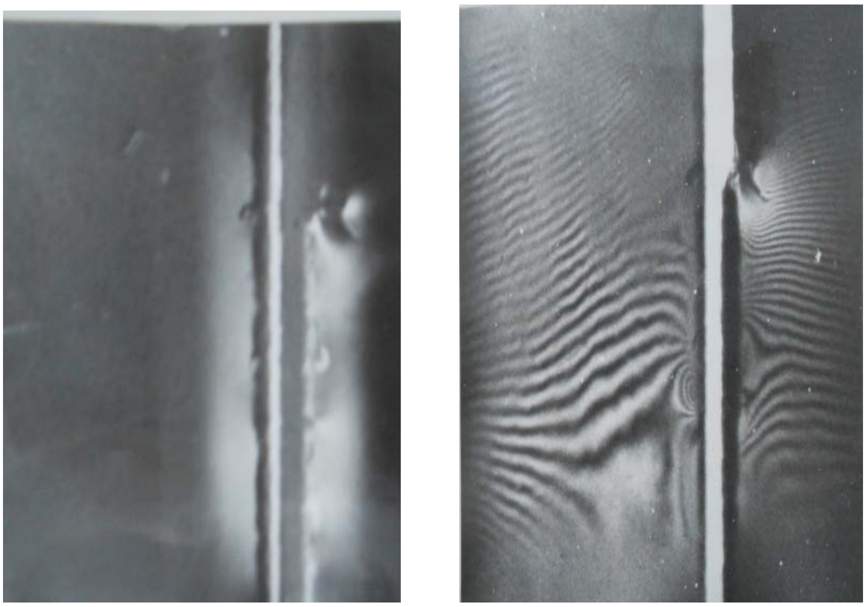
It is known that during the surface machining with a free abrasive material, the structure and depth of the damaged layer are determined by physical and mechanical properties of the processed crystal and abrasive grains. The study of the structure defects, which occurred on different surfaces of semiconductor single crystals, was carried out repeatedly by optical and electron microscopy and X-ray diffraction topography methods [1 – 6]. It can be observed that the plastic deformation generally occurs during the surface polishing, and the brittle fracture takes place during cutting and polishing processes.



a) b)

Fig. 1. Moire pattern of analyzing crystal cut, reflection $(\bar{2}20)$: a) before etching; b) after etching ×12.

Interferometers were previously studied. The interferometer, which was used for the analyzing crystal cut and aperture, had a rotational moire, which corresponds to the lower part of Figure 1, 2*b*. Experimental diffraction moire patterns obtained with the interferometer cut and aperture made by an inner side of the diamond disc perpendicular to the analyzer plane (111), are shown in Fig. 1, 2, received in $CuK\alpha$ - radiation using reflections ($\bar{2}20$). The moire patterns represent predominantly rotational moire.



a) *b)*

Fig. 2. Topograms and moire pattern of analyzing crystal aperture. Reflection ($\bar{2}20$)
a) topograms from analyzing crystal aperture; b) moire pattern from analyzing crystal aperture ×12.

The cracks of 30 – 40 μm deep occur on the crystal surface after cutting. The aperture width was about 235 μm. The front cutting edge of the disc has sharp projections that will serve as concentrators of mechanical stresses and microcracks.

It is known that the largest damages to the surface of the crystal arise in the process of its cutting with a diamond disc. As a result of the impact stress that occurs in the cutting process, irregularities, traces of plastic deformation and brittle fracture are observed on the surface. Three specific dependences of the period of moire fringes on the deformation size can be differentiated in diffraction moire patterns: dilatation moire – $\Lambda_d = \dfrac{d_0 d}{|d - d_0|} = \dfrac{1}{\Delta g}$, rotating moire – $\Lambda_r = \dfrac{1}{\Delta g_r} = \dfrac{d_0}{\theta}$ and mixed moire – $\dfrac{1}{\Lambda} = \sqrt{(\dfrac{1}{\Lambda_d})^2 + (\dfrac{1}{\Lambda_r})^2}$, Δg_r – change in diffraction vector, g – diffraction vector, d_0 – interplane lattice distance, d – interplane distance of deformed lattice. By measuring the periods of moire fringes and their inclination relative to reflecting surfaces by means of relations:

$$d = \Lambda[1 + (\frac{\Lambda}{d_0})^2 + 2\frac{\Lambda}{d_0}\cos\varphi]^{\frac{1}{2}},\ \theta = \frac{\sin\varphi}{\dfrac{\Lambda}{d_0} + \cos\varphi}$$

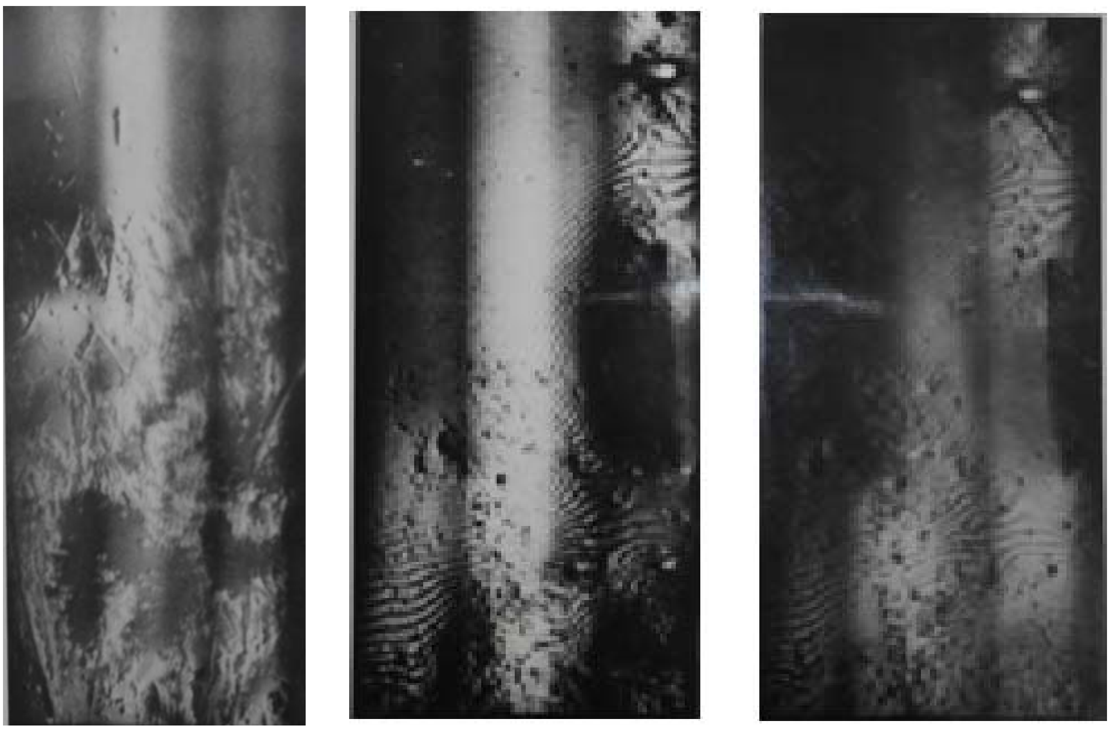
the relative deformations $\Delta d/d_0$ and atomic plane turns θ in the analyzing crystal were calculated. The relative deformations vary from 3×10^{-6} to 0.17×10^{-6} and atomic plane changes – from 0.0032 to 0.25 arcsec.

It can be seen from the moire patterns and topograms (Fig. 1) that the area, in which moire fringes are not present, is 125 μm from the edge of the aperture, due to violation of the coherence of interfering waves. In the moire pattern at a distance of more than 125 μm, a large distortion area is observed, which includes dislocations and no moire fringes, because the distance between them is very small at the boundary of film resolution (Fig. 1, 2*b*). Beyond this zone, dislocations manifested in the form of additional moire fringes are observed.

It follows from the analysis of the relative deformations and atomic plane changes that the fields of elastic deformations expand at a distance of about 700 – 1000 μm. In addition to X-ray interferometric studies, X-ray topographic studies were conducted using three-crystal Laue spectrometer (one was made of interfering beams covered with an opaque screen). Fig. 2*a* shows a topogram obtained in a three-crystal Laue spectrometer circuit. It follows from interferograms and topograms that the defective structure, which occurs during crystal cutting, is generally composed of a strongly deformed area of the crystal matrix. These areas are manifested in the form of black and white lobes (Fig. 1, 2). These fields expand to a large depth – hundreds of microns.

The paper proposes a method for determining the sign of deformation. For this purpose a thermoelement was used, which made it possible to form the temperature gradient along the atomic planes ($\bar{1}10$) in the direction of [$11\bar{2}$], the value of which was 1.2 K/cm, as shown in [9].

The homogeneous temperature gradient proves the stability of thermoelement operation, since the exposure period of obtaining moiré patterns lasted almost 5 hours. The temperature gradient will increase interplanar distances in the analyzer. The analysis of interferograms shows that the deformation in the crystal aperture area is the tensile deformation. The increase in periods also testifies to the nonuniform distribution of elastic deformation fields.



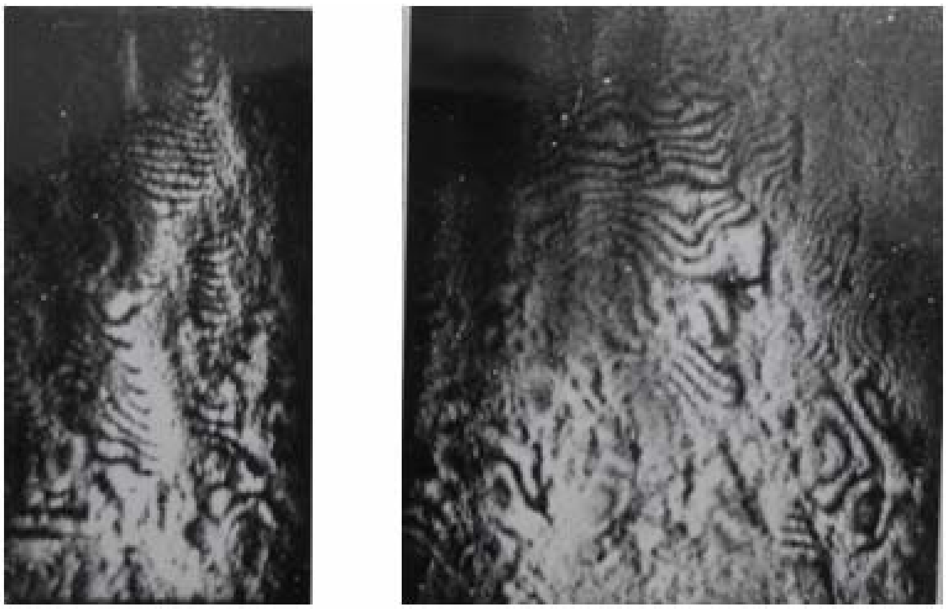
a) b) c)

Fig. 3. Interferograms and topograms of partially processed surface of analyzing crystal: a) topogram, reflection ($\bar{2}20$); b) interferogram in the direction of diffracted beam; c) in the direction of the incident beam ×12.

With the partial processing of the original surface (111) of the interferometer analyzer with emery powders with grain size of 5 μm, scratches, chips with sharp edges, microcracks, etc., are observed in the topogram (Fig.3*a*) (the topogram was obtained in three-crystal LLL-spectrometer circuit). In some places, where the surface is not damaged by abrasive materials, the areas with the reduced intensity are observed (in Fig. 3*a* an opposite contrast relative to a photoplate), which testify to the presence of nonrelaxing elastic distortions in the crystal.

It can be seen from the moire patterns (Fig. 3*b*, *c*) obtained using the three-crystal interferometer that the surface microdamage significantly distorts it. The periods and inclinations of the moire fringes vary in wide ranges, as well as their disappearance in some areas testify to nonuniform stress distribution across the wafer area. The reduced intensity areas occur in some places (Fig. 3*a*), where the deformation equals to 10^{-5}. These areas are characterized by contrast addition in the direction of the incident beams (Fig. 3*b*) and diffracted (Fig. 3*c*) beams.

With a uniform polishing of the analyzer surface (111), an attempt to obtain the moire pattern was unsuccessful. The high density of defects and large stresses in the crystal completely destroy the interference interaction of X waves. It is worth noting that the low-temperature annealing at 700 K had had no positive effect as well. After the annealing of the interferometer at 1123 K, the moire pattern shown in Fig. 4 was obtained.

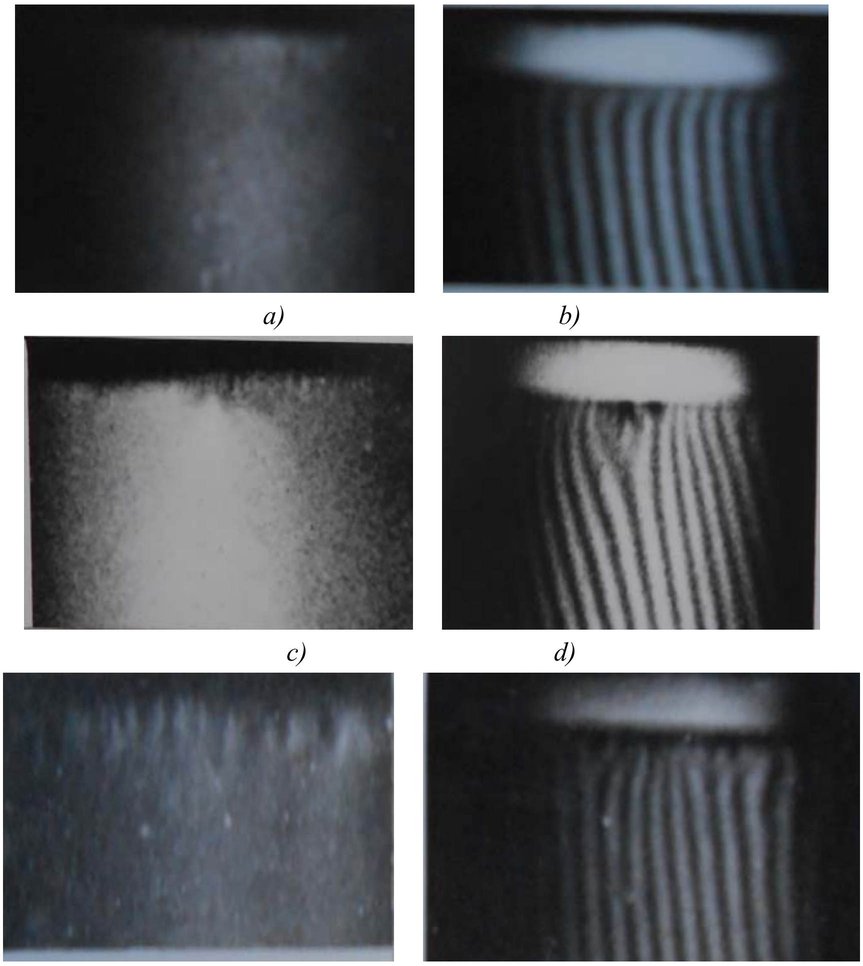


a) *b)*

Fig. 4. Moire patterns obtained from different parts of the crystal after annealing at 1123 K. *Reflection* $(\bar{2}20)$ *×12.*

The analysis of the moire patterns shows that the stress distribution becomes more uniform. The deformation in the crystal varies from 10^{-5} to 10^{-6}. Almost all irregularities in the periods of moire fringes are detected in the moire patterns: additional moire fringes, fork-like lines, crosslines between fringes, shifts of several fringes, etc. This is most likely associated with the reconstruction of the damaged layer and formation of dislocations, as evidenced by the presence of additional moire fringes. Most dislocations are straight-line, lying in {111} planes. The low-temperature stage of stress relaxation in mechanically damaged layers is accompanied by conservative movement of dislocations. Similar defects were observed earlier during the machining of crystals [6, 11]. After etching of the damaged layer 10 μm thick, more distinct moire fringes were observed. Therefore, dislocation dipoles, packing and other defects are detected in the subsurface layer. Dashed lines of the diffraction contrast mostly oriented in the direction of $[11\bar{2}]$ (Fig. 4*a*, *b*), fields of elastic deformations lead to the bending of moire fringes. Obviously, dashed lines correspond to dislocations oriented along this direction $[11\bar{2}]$. The dislocations of this type were detected by electron microscopy in [1, 2, 11]. In the presented interferograms, individual microcracks are observed in the form of dark lines oriented in different directions, from which short moire fringes extend (the pattern is similar to the X-tree branches). The deformations located in close vicinity to residual microcracks can be defined from the moire patterns.

The study of the damaged layer depth, which greatly depends on the size of abrasive grains, is of particular interest. For this purpose, the polishing with various abrasive materials was carried on the end surface of the analyzer wafer that corresponded to the crystallographic plane $(11\bar{2})$. The assessments of the damaged layer depth were also conducted by optical microscopy. X-ray topograms and interferograms obtained during diffraction from the planes $(\bar{2}20)$, are shown in Fig. 5*a*, *b*, *c*, *d*, *e*, *f*. When polishing with abrasive material M-5 (Fig. 5*a*, *b*), some cracks and areas of high scattering intensity can be seen in topograms; interferograms along with usual topographic images show the change of the original moire pattern, indicating the emergence of the elastic deformation area. The depth of the damaged layer is 15 – 20 μm (together with an area of elastic deformations).



a) *b)*

c) *d)*

e) *f)*

Fig. 5. Topographic and moire images of the damaged layer depth. Reflection $(\bar{2}20)$ a) b) surface machine processing $(11\bar{2})$ with M5 powder; c) d) with M10 powder; e) f) with M28 powder ×12.

If the abrasive material size is 10 µm (Fig. 5*c*, *d*) black and white lobes of deformation rosettes and a sufficiently large area of elastic deformations begin to appear in topograms, and additional fringes or their splits, as well as an essential region of elastic deformations over long distances, are observed in the moire patterns. The depth of the damaged layer is 35 – 40 µm. If the abrasive material size is 28 µm (Fig. 5*e*, *f*), the number of deformation rosettes and irregularities in the moire patterns increases. The damaged layer depth is approximately 120 – 140 µm. In terms of X-ray diffraction, the damaged layer can be divided into two zones: of kinematic and dynamic scattering. The kinematic scattering is observed from the polycrystalline part of the damaged layer - from the zones of dislocation ensembles and elastic deformations.

As a result of the studies conducted by the optical microscopy, X-ray topography and X-ray diffraction moire methods, the damaged layer model can be represented as follows: *a*) a relief zone with polycrystalline structure, from which the kinematic scattering is observed; this zone is best determined by the optical microscopy method, and its approximate dimensions are 0.2 – 0.5 *d* (*d* – abrasive material grain size); *b*) a zone of microcracks, packing defects and dislocation ensembles, which is well defined by the electron microscopy, X-ray diffraction moire and X-ray topography methods (optical microscopy methods are not used here), the zone depth varies in the range of 3 – 4 *d*; *c*) an elastic deformation zone; in this area, X-ray diffraction moire method has advantages over all other known methods, since the sensitivity of X-ray diffraction moire method to lattice distortion is 10 times higher than of the electron diffraction moire method, and the depth of the damaged area is 4 – 5 *d*. The values of deformations and stresses in the second and third zones can be reliably determined by the X-ray diffraction moire method. The discrepancy in the received data on determining the damaged layer depth in the latter zone is the most significant in comparison with known measurements reported in literature [1, 2].

Conclusions

A new method of determination of the damaged layer depth in the silicon single crystals using X-ray diffraction moire was proposed. A refined model of the damaged layer, consisting of: *a*) a relief zone with polycrystalline structure, from which the kinematic scattering as large as (0.2 – 0.5 *d*) is observed; *b*) a zone of microcracks, packing defects and dislocation ensembles of (3 – 4 *d*); *c*) an elastic deformation zone with an area of (4 – 5 *d*). This elastic deformation zone is quite long, even during the removal of the first two zones the residual stresses in the crystals still remain.

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