
V.P. Shafraniuk

V.P. Shafraniuk

Higher Educational Establishment of Ukraine
Bukovinian State Medical University, 2 Teatralna Square,
Chernivtsi, 58000, Ukraine

RESEARCH ON MECHANICAL STRESS RELAXATION IN REAL CRYSTALS BY X-RAY DIFFRACTION MOIRE METHOD

The paper presents the results of research on the strain fields arising in the vicinity of local damages in silicon and germanium single crystals using X-ray diffraction moire method. It is established that relaxation of strain fields around mechanical damages (indenter marks and scratches, laser induced damages) takes place even at room temperature, as well as at annealing temperatures from 473 K to 1073 K. Low-temperature relaxation results from atomic displacement due to weakening of chemical bonds, whereas high-temperature relaxation results from dislocation motion in {111} planes and <110> *directions.*

Key words: scratches, indenter marks, X-ray interferometer, moire fringes, thermoelement, thermal cooler.

Introduction

A relevant problem in thermoelectricity is creation of high-quality and reliable metal-thermoelectric material ohmic contacts. The quality and reliability of such contacts is influenced by structural perfection of near-surface layers of thermoelectric materials. In most cases, a metal layer-thermoelectric material structure comprises areas of local mechanical stresses that are related to interface boundaries and local damages of material surface [1]. Thermal treatment stipulated by technology of creating contacts to high-temperature thermoelectric materials based on germanium-silicon solid solutions leads to relaxation of local mechanical stresses and formation of dislocation clusters [2]. Physical regularities of the process of relaxation of mechanical stresses in planar contact structures allow solving the problem of preservation of structural perfection of thermoelectric materials, which is a prerequisite for creation of high-quality and reliable contacts in thermoelectric materials. With modern microminiaturization of semiconductor devices and thermoelectric modules it is necessary to know the distance at which working components should be arranged from the scribed stripes, as long as strain fields affect the electric parameters of these devices. The data on the dynamic properties of dislocations in semiconductors were mainly obtained from measuring the velocity of dislocations [2] under the effect of time-constant stress, whereas formation of defects in real semiconductor structures occurs in variable stress field. In [2], by X-ray topography methods it was established that during scribing strain fields have a length of ~ 100 – 150 μm.

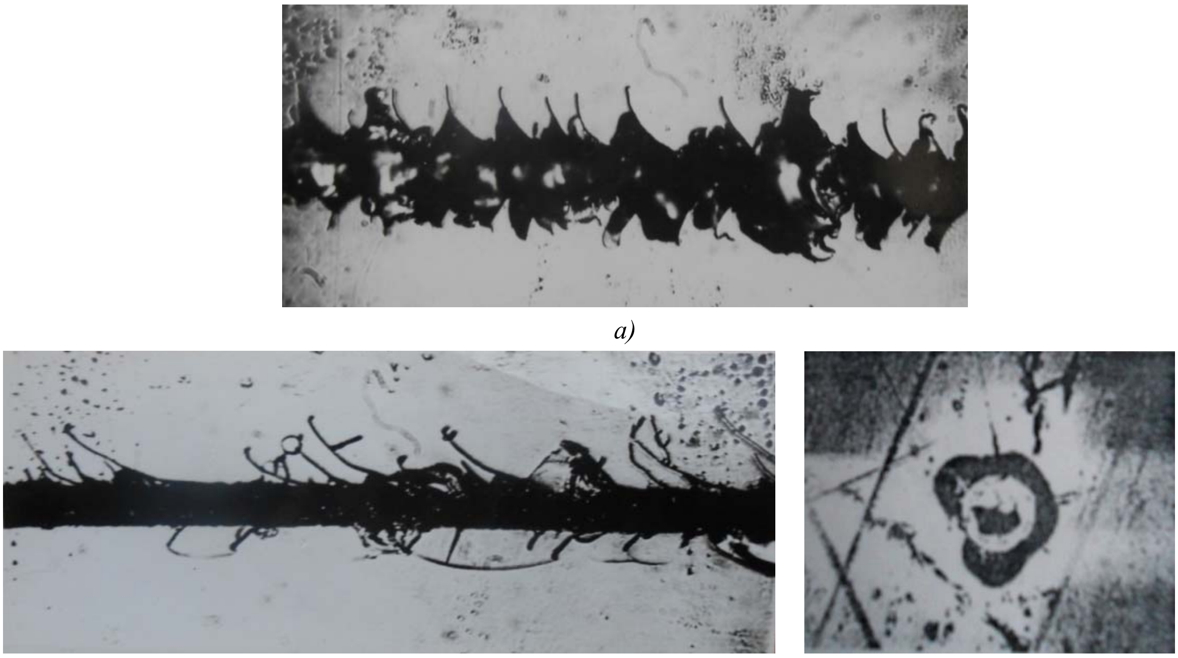
Thus, the research on the process of relaxation of local mechanical stresses is of great current interest. X-ray diffraction moire (XRD) method is exceptionally sensitive to slight strains ($10^{-4} – 10^{-8}$) and relative rotations ($0.1 - 0.001''$) of atomic planes and makes it possible to measure with high accuracy the absolute values of wavelength and periods of crystal lattices, to determine refraction factors and dispersion corrections of various substances, to study the heterogeneity of thermoelectric solid solutions *Ge-Si*, *Bi-Te*, biological objects with phase moire topography, to determine the Burgers vector of single dislocations [3 – 8]. In its universality, XRD method outperforms considerably all known X-ray diffraction methods. Exactly for this reason the present paper employs XRD method to study the relaxation of strain fields in real crystals which occur around local damages (indenter marks, scratches, laser induced damages – craters) in the surface layers of silicon and germanium at different annealing temperatures.

Research methods

Research was performed on interferometer samples made of perfect silicon and germanium single crystals. Prior to causing local mechanical damages on the output surface of the analyzing crystal, interferometers had been investigated. Some interferometers under study partially comprised structural moire fringes and were moire-free, i.e. perfect. Local mechanical damages in the surface layers on the output surface of silicon, germanium analyzing crystal of (111), (100), (110) orientation were simulated with the aid of microhardness indenter marks, scratches and laser induced damages. Moire patterns were obtained in CuK_{α}-radiation using a scanner along the diffraction vector. Marks and scratches were applied by a diamond indenter on micrihardness tester on the output surface of the interferometer analyzing crystal in different crystallographic directions at different loads. Laser surface damage manifested in the form of a crater, was made by means of neodymium laser on the surface of analyzer (111).

Research results

During scribing of a scratch two processes should be distinguished: impression and indenter motion along crystal surface. A zone of plastically strained material permeated with microcracks and chips, as well as a zone of elastic stresses related to riveting are created in the vicinity of a scratch. The strained area in the vicinity of microindenter marks and scratches can be found from moire patterns [5].

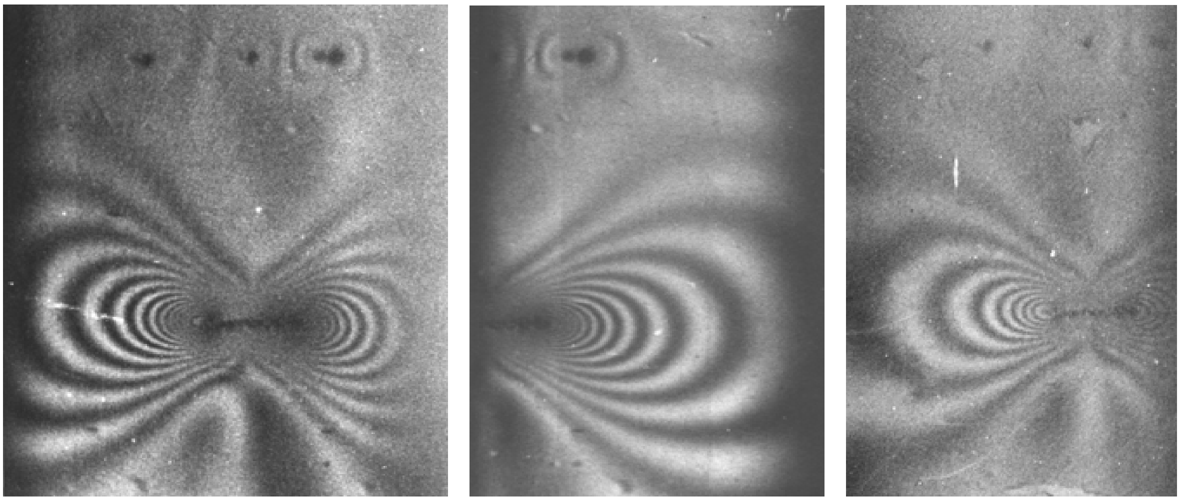


a)

b) *c)*

Fig. 1. Appearance of scratches in different crystallographic directions on the surface of analyzer: a) in [110] direction, b) in [$11\bar{2}$] direction, c) image of laser induced damage on (111) surface.

Fig. 2 shows a moire pattern from a scratch and indenter marks at different loads 15, 20, 25 g applied on the output surface of the analyzing crystal of perfect silicon interferometer. The direction of a scratch coincides with the direction of the diffraction vector g at a load of 25 g and length 2 mm. Moire patterns were obtained with the aid of a scanner in CuK_α-radiation along the diffraction vector. Moire fringe is symmetrical with respect to the centre of a scratch divided by zero moire fringe corresponding to the resulting strain field from the scratch. To the left and right of the zero fringe there are 12 – 14 moire fringes the distance between which with approach to the edges of a scratch is reduced, which allows speaking about strain increase. It is known that a moire fringe is a geometrical place of points of equal displacements along the diffraction vector, since as at the distance equal to moire fringe period the value of displacement is equal to interplanar distance of perfect lattice. An interferogram was also obtained from this scratch at rotation of interferometer by 90 degrees with the use of reflection $(0\bar{2}2)$, when the diffraction vector is normal to this scratch. Scratch image on the moire pattern is an intermittent light line restricted on both sides by a dark halo, and a diffraction contrast from a scratch (Fig. 2), when the diffraction vector is parallel to it, is composed of black and white lobes. Moire fringes envelop the scratches.



a) *b)* *c)*

Fig. 2. Moire patterns from the scratch and indenter marks obtained from different areas of interferometer analyzer in CuKα radiation at room temperature (a, b). b) after annealing at temperature 673 K. Reflection $(0\bar{2}2)$*, ×10.*

On moire patterns (Fig. 2) one can simultaneously observe diffraction images of the scratch and indenter marks, localized next to them and long-range strain fields in the form of moire fringes. From the moire patterns it is seen that elastic strain fields of indenter marks expand to large distances which many times exceed their real dimensions *d*. The defined dimensions of contrast areas *D* along the diffraction vector allow speaking about their asymmetry. The asymmetry line of diffraction contrast with respect to reflection planes coincides with zero contrast line perpendicular to the diffraction vector. Reducing the load and indenter mark size, we managed to show that the ratio of contrast value to indenter mark size increases and this is most probably due to peculiarities of stress relaxation in the surfaces layers of silicon. Decrease in *D*/*d* with increasing the load and indenter mark size is attributable to the onset of brittleness limit in silicon crystal under the indenter and the relief of residual stresses in the process of occurrence of microcracks.

Fig. 2 shows a moire pattern at interferometer annealing at temperature 673 K in the air. From the moire patterns (Fig. 2) it is seen that partial stress relaxation takes place in the vicinity of indenter marks and scratches.

On the diffraction moire patterns there are three typical dependences of moire fringe period on strain value: $\Lambda_d = \frac{d_0 d}{|d - d_0|} = \frac{1}{\Delta g}$ - dilatation moire, rotation moire - $\Lambda_r = \frac{1}{\Delta g_r} = \frac{d_0}{\theta}$, mixed moire – $\frac{1}{\Lambda} = \sqrt{(\frac{1}{\Lambda_d})^2 + (\frac{1}{\Lambda_r})^2}$. Measuring the periods between moire fringes and their inclination to reflecting planes by means of relations:

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

we calculated relative strains $\frac{\Delta d}{d_0}$ and rotations of atomic planes θ in the analyzing crystal. Relative strains change from 2 × 10^{-6} to 5 × 10^{-7}, and rotations of atomic planes – from 0.0025 to 0.05 angular seconds.

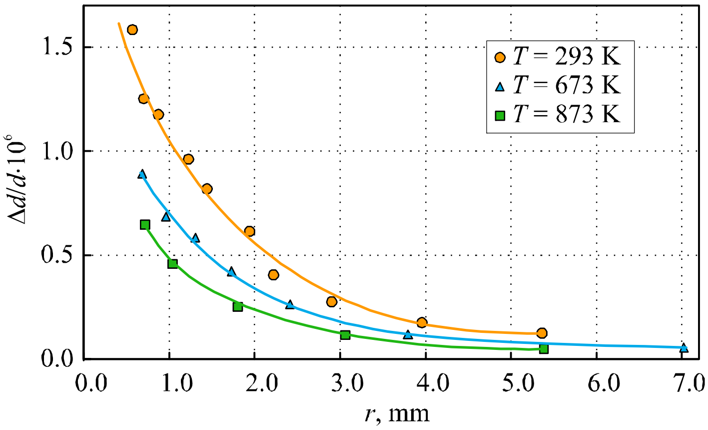
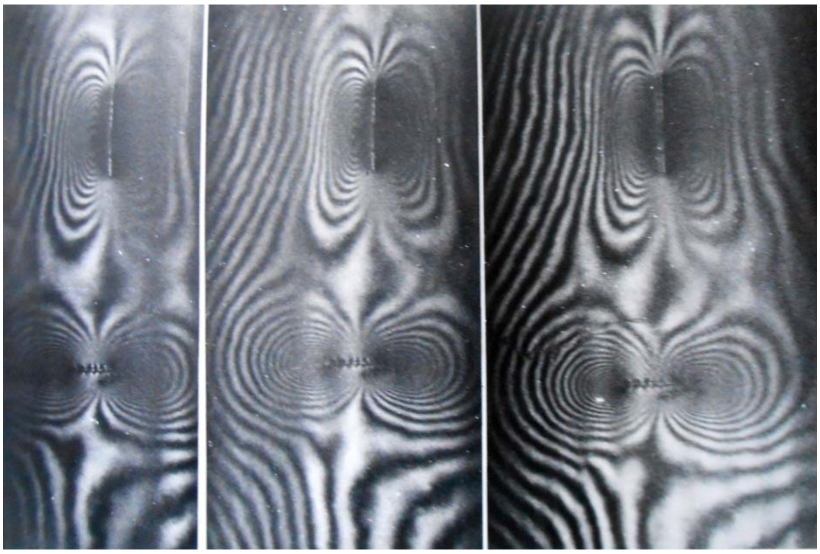


Fig. 3. Curves of relative strain versus the edge of a scratch (Fig. 2).

Fig. 3 represents curves of relative strain versus the distance from the edge of a scratch for different annealing temperatures. Analysis of the investigations shows that stress relaxation processes in silicon crystal at annealing temperatures from 293 K to 873 K are based on different mechanisms: 1) initial stress relaxation as a result of atomic displacement due to weakening of chemical bonds with a rise in temperature; 2) high-temperature relaxation occurs due to dislocation motion in {111} planes and <110> directions [5].

The paper also studied the way scratches are depicted in structural dilatation moire which are scribed in different directions to the diffraction vector (Fig. 4). These interferograms (Fig. 4) were obtained from a silicon interferometer, on the output surface of which two scratches 1.5 mm and 2 mm were scribed parallel and normal to the diffraction vector g_{220}, respectively, under the load of 40 g.

Structural moire fringes are moved apart by the field of elastic strains that appeared in the area of scratches. In the moiré patterns (Fig. 4), the structure of the diffraction contrast of scratches is clearly visible. Interferograms obtained at different times (1, 5, 12 days, Fig. 4), allowed revealing that even at room temperature there is stress relaxation around scratches, which is manifested in contrast change, splitting of moire fringes and change of period between them. It is almost impossible to fix this change by other methods, since a change in strained crystal area near the scratch has passed interplanar distance (1.920752 Å).



a) b) c)

Fig. 4. Moire patterns of scratches on (111) surface of Si analyzer in [110] and $[11\bar{2}]$ directions at a load of 0.4 N: a – 1 day after scratching; b – 5 days; c – 12 days, ×8.

The number of additional moire fringes around a scratch depends on the load on the indenter (Fig. 4, 5). Structural moire fringes in the centre of a scratch are divided by zero dark moire fringe relative to which the moire pattern is partially symmetric (Fig. 5).

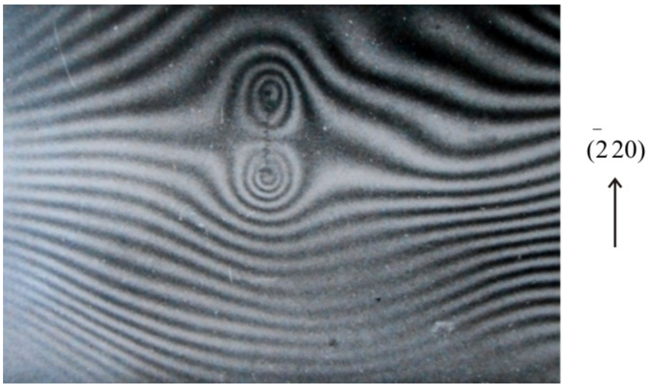
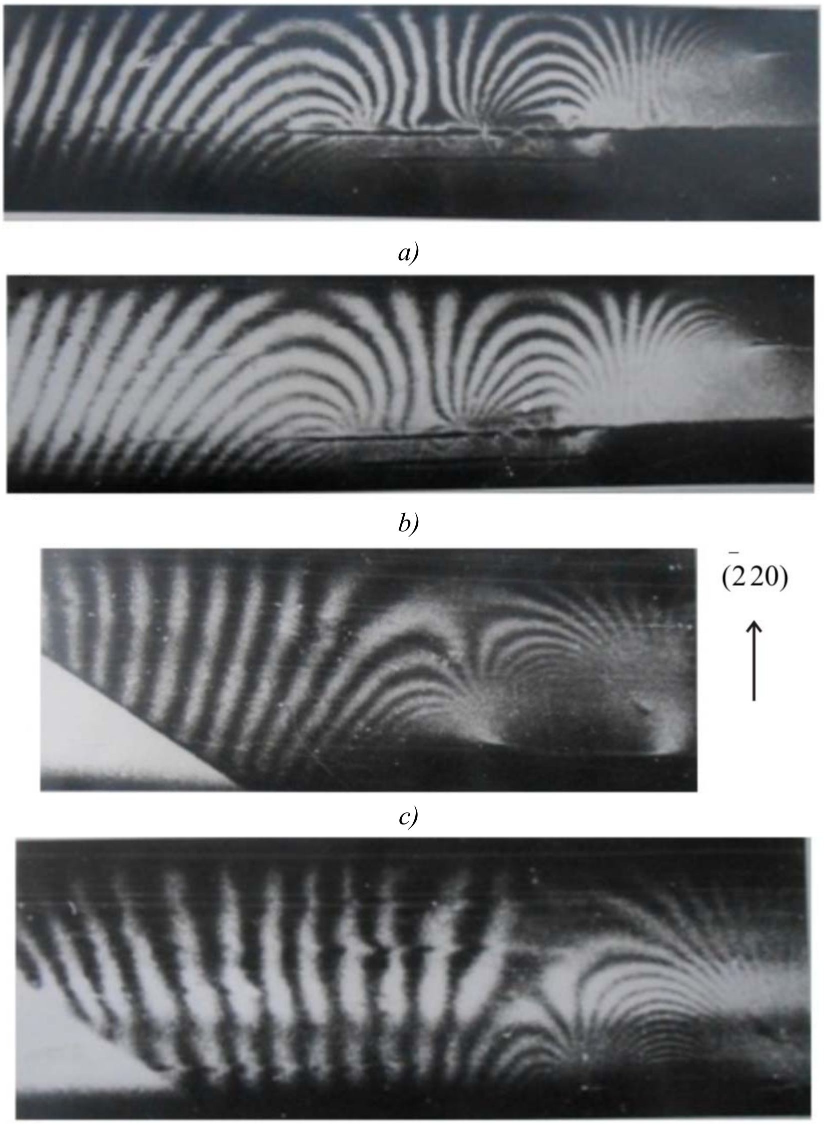


Fig. 5. Image of a scratch in the structural moire applied on the analyzer surface (111) in $[\bar{1}10]$ direction at a load of 0.15 N. Reflection $(\bar{2}20)$, ×8.

It is noteworthy that on the interferograms one can simultaneously observe a diffraction image of the scratch which is localized close to it and to strain fields which become apparent as moire fringes at large distances. The dimensions of diffraction and moire contrast areas *L* tens and hundreds of times exceed the geometrical dimensions of scratches. With increasing scratch width, the ratio *L*/*d* (*d* is scratch width) is reduced. This is due to the fact that under the influence of large loads the boundary of brittle fracture occurs, causing the appearance of cracks and partial relaxation of elastic stresses.

This paper also analyzed the way a scratch is depicted depending on its depth in diffraction moire pattern. For this purpose an interferometer was used which comprised a rotation moire according to which the relative rotation of atomic planes corresponded to 0.025 sec. The interferometer analyzer was set at an angle of 30 minutes in drawing plane, as a result of which the indenter was buried in the surface.

Fig. 6 shows moire patterns with two scratches scribed on the analyzer plane (110) in [001] direction. Diffraction vector g $(\bar{2}20)$ is normal to traces of scratches. The resulting total field of elastic strains from the two scratches is located on one side of them.



a)

b)

c)

d)

Fig. 6. Interferograms of the system of scratches: a, b – scratches on (110) surface of Si analyzer in [001] direction; c, d – relaxation of stresses after після breaking of plate along the scratch line. Reflection $(\bar{2}20)$ *×10.*

Seven closest to the scratch moire fringes from the perfect crystal part bend and end near the scratch. Seven further moire fringes begin on the scratch, bend and after some time end on it, which testifies to alternating-sign character of bend of atomic planes. With slight bends of interferometer analyzer, the location of moire fringes is changed, the contrast of moire fringes is changed, but the structure of strain field remains unvaried (Fig. 6*b*). In this case, strain area found from the moire patterns (Fig. 6), in [110] direction reaches 1 mm. After breaking of analyzer plate along scratch line, the strain area decreased to 0.45 mm, as long as stress relaxation took place as a result of change in the moire patterns (Fig. 6*c*, *d*). The strained area of the analyzing crystal was displaced by interplane distance, as long as the contrast of moire fringe changed to the opposite. On the moire pattern (Fig. 6*d*) in the bifurcated moire fringe one can observe 12 additional fringes, pointing to the presence of dislocations, since each additional fringe corresponds to a dislocation.

From this system of scratches a moire pattern was also taken with the use of reflection (004), when the diffraction vector was parallel to scratch lines (Fig. 7).

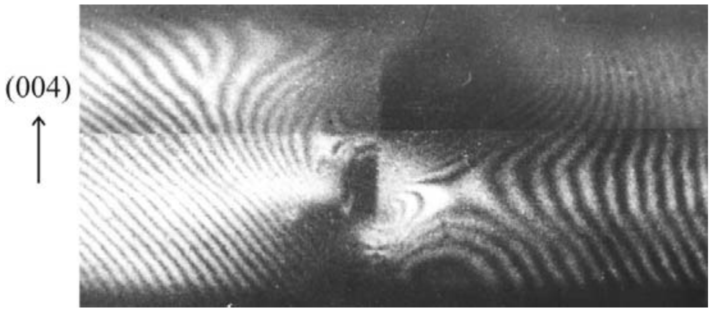
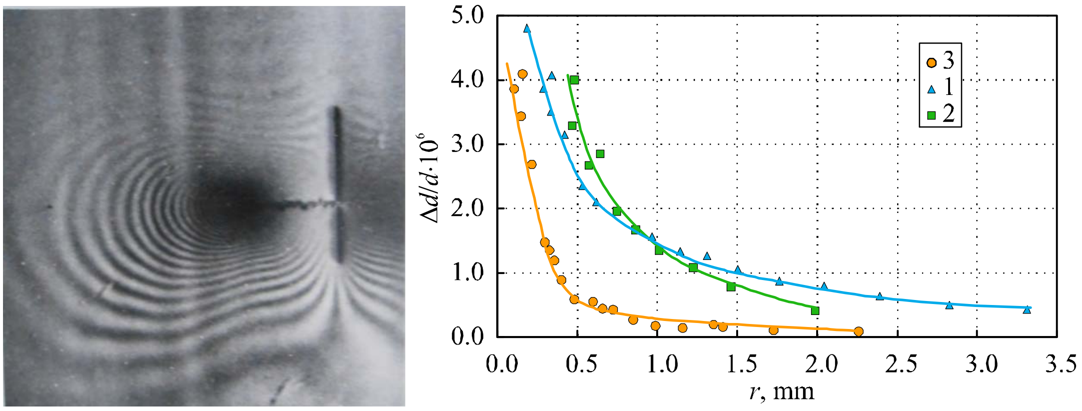


Fig. 7. Interferogram of scratches, reflection (004, ×10.

The number of additional fringes near the scratch per unit length is large. The upper part of the interferogram shows a dislocation in the form of two additional semi fringes. The number of additional fringes in moire pattern N is determined by the projection of the Burgers vector to the normal to reflecting planes $N = (qb)$, for full dislocations N is an integer, and dislocation in moire pattern becomes apparent as one or several additional fringes.

Of particular interest is investigation of strain fields arising near the intersection of two scratches. Such scribing method is widely used in the fabrication of microcircuits. It was demonstrated above that strain fields are essentially dependent on the orientation of scratch lines relative to crystallographic directions. For this case scratches were scribed on the output surface (111) of perfect germanium interferometer analyzer at a load of 0.15 N in [110] and $[11\bar{2}]$ directions.

As is seen from Fig. 8, the character and value of atomic plane strains depends on the distance to the strain and its orientation relative to diffraction vector. The resulting moire pattern from two scratches which intersect is a system of moire fringes which envelop a scratch parallel to diffraction vector and end on a scratch parallel to it.



a) *b)*

Fig. 8. a – interferogram of intersecting scratches in $[\bar{1}10]$ and $[11\bar{2}]$ directions, reflection $(\bar{2}20)$, ×10, b – relative strain of atomic planes versus the distance from the edge of scratch in $[\bar{1}10]$ direction:

1 – [110], 2 – $[11\bar{2}]$, 3 – $[\bar{1}10] \wedge [11\bar{2}] = 45^\circ$.

Fig. 8*b* represents the curves of dependence of relative strains of atomic planes on the distance to the scratch in different directions. The dependence of relative strain of atomic planes on the distance to the scratch corresponds to function -1/*r* (*r* is the distance from the edge of the strain), which testifies to dislocation structure. The structure of displacement fields is practically unchanged in the presence in the interferometer of dilation, rotation or phase moires.

The paper also examines how a more pattern is formed from the scratches applied at different angles to the diffraction vector (Fig. 9) in structural moire. The resulting strain field becomes apparent in additional moire fringes which begin on one scratch and end on the other, the number of such additional fringes is almost 14.

a) *b)*

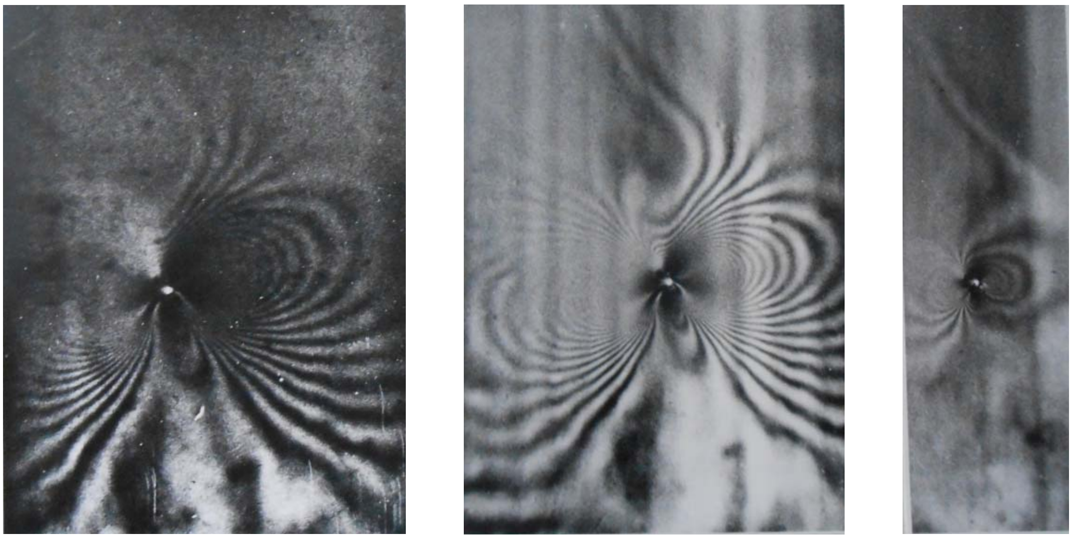
Fig. 9. Image of scratches applied at an angle to diffraction vector $g_{\bar{2}20}$ *:*
a) at room temperature; b) after annealing at 1023 K, ×10.

Annealing of interferometer at 1023 K leads to relaxation of stresses in the area of scratches, owing to which the number of moire fringes reduced to three, and relative strains of atomic planes reduced by an order of magnitude. High-temperature relaxation of stresses around scratches occurs due to motion of dislocations in {111} planes and <110> directions.

Note that the paper considered the impact of temperature gradient created in the interferometer on the formation and appearance of moire patterns when it is higher and lower than zero. In the former case the interferometer was heated to 310 K by means of thermoelement, in the latter – it was cooled by means of thermal cooler to 263 K. High-quality and contrast moire patterns could not be obtained from different scratches, as long as interacting waves in the interferometer analyzer are not completely coherent, owing to which there is a relationship between the amplitudes of the waves and their phases in the first two interferometer components (*S* and *M*).

An important aspect of the investigation is to determine strain fields which arise at interaction of focused laser beam with the surface of silicon single crystals, as long as laser beam scribing is widely used in semiconductor industry when breaking plates into elements [1]. When silicon surface is exposed to a laser beam, craters are formed only when radiation intensity exceeds critical value and in separate cases they have the shape of a hexagon (Fig. 1*c*) in (111) plane.

Fig. 10 represents interferograms from laser induce damage which are symmetrical relative to direction $[11\bar{2}]$. From the moire patterns it is seen that elastic strain fields expand to long distances which are in large excess over the geometrical dimensions of damages and the diffraction contrast. Imposing temperature gradient $dT/dy = 2$ K/см on the interferometer analyzer by means of thermoelement along the atomic planes $(\bar{1}10)$ [7], it was shown that stress relaxation occurs even at room temperature (Fig. 10*b*). This low temperature gradient in the interferometer analyzer leads to relaxation of stresses, as testified by the increased contrast of moire fringes (Fig. 10*b*) and high stability of thermal cooler (thermoelement), as long as the exposure of moire patterns lasted almost 6 hours. Using relation (1), the relative strains $\frac{\Delta d}{d_0}$ and rotations of atomic planes θ in the analyzing crystal in the vicinity of laser induced damage were calculated. At annealing of interferometer at different temperatures we managed to find out the processes of relaxation of stresses in the area of laser damage. At annealing temperature 1273 K there is considerable reduction of crystal strain which is clearly visible from the interferogram (Fig. 10*c*). Calculations showed that relative strains decrease by about 16 times, and the structure of strain field remains unchanged. Control and investigation of structural perfection and distribution of strain fields in the vicinity of local damages allows one to control the energy of laser radiation and correct its technological modes.



a) *b)* *c)*

Fig. 10. Moire pattern of laser induced damage in CuKα-radiation with the use of reflection $(\bar{2}20)$*:*
a – after laser induced damage; b – after applied temperature gradient; c – after annealing, ×10.

X-ray diffraction (XRD) moire method allows one to determine with high accuracy the long-range displacement and strain fields of crystal atomic planes at considerable distances from the system of scratches and laser damages, thereby reproducing the real function of local misorientations of the strained crystal region which can be used for theoretical calculation with the use of the Takagi equations of moire patterns [8].

Conclusions

A new method was proposed to determine strain field distribution in the vicinity of local damages in silicon and germanium single crystals with the use of X-ray diffraction moire. It was found out that relaxation of strain fields around mechanical damages (indenter marks, scratches and laser craters) occurs even at room temperatures, as well as at annealing temperatures from 473 K to 1273 K. Low-temperature relaxation results from atomic displacement due to weakening of chemical bonds, and high-temperature relaxation results from dislocation motion in {111} planes and <110> directions. Knowing strained area from the scribed stripes, one can correctly design integral circuits, arranging their components not closer than 150 μm from the edge of the scratch.

References

1. O.A. Kontsevoy, Yu.M. Litvinov, and E.A. Fattakhov, *Plasticity and Strength of Semiconductor Materials and Structures* (Moscow: Radio i Sviaz, 1982), 240.
2. S.S. Gorelik, Yu.M. Litvinov, and A.V. Prikhodko, Relaxation of Local Mechanical Strains in Silicon Near-Surface Layers, *J. Surface Investigation* 5, 80 – 83 (1985).
3. N.D. Raransky, V.P. Shafraniuk, and I.M. Fodchuk, X-ray Interferometric Image of Strain Fields around Dislocation Clusters, *Metal Physics* **7(**5), 63 – 71 (1985).
4. N.D.Raransky, V.P. Shafraniuk, Defects of Interface Boundaries and Stress Relaxation of *Si*-*Si*, *Ge*-*Si*, *GaP*-*Si* Epitaxial Systems, *Ukrainian J. Physics* 30 (1), 127 – 132 (1985).
5. V.P. Shafraniuk, Potential of X-Ray Diffraction Interferometry in Studying the Relaxation of Local Mechanical Stresses in the Subsurface Layers of Single Crystals, *Scientific Bulletin of Chernivtsi National University, Physic*s, issue 32, 122 – 127 (1998).
6. N.D. Raransky, Ya.M. Struk, I.M. Fodchuk, V.P. Shafraniuk, and A.N. Raransky, Applied Possibilities of X-Ray Diffraction Interferometry, *Proc.SPIE -Bellingham* 2647, 457 – 467 (1995).
7. V.P. Shafraniuk, Determination of Structural Changes and Temperature Distribution within Crystals, *J.Thermoelectricity* 3, 89 – 94 (1998).
8. I.M. Fodchuk, M.D. Raransky, Ya.M. Struk, I.V. Fesiv, et al., Moire Images of Defects in X-ray Three-Crystal Interferometry, *Scientific Bulletin of Chernivtsi National University. Physics,* issue 92, 14 – 19 (2000).

Submitted 04.11.2016