THE MICROMECHANICAL PROPERTIES OF GaP SINGLE CRYSTALS EXPOSED TO PULSED LASER IRRADIATION

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Abstract

The results of pulsed laser radiation action (UV region) on the mechanical properties (microhardness, fragility, density, and behavior of dislocations) of GaP crystals are presented. It is established that the action of laser radiation *in situ* generally results in the hardening of the surface layer of irradiated samples: their microhardness increases. It is also found that the effect of laser irradiation is of long duration (reaching sometimes several days) and causes an aftereffect. During this long process, alternating modifications of microhardness are observed: a decrease and increase in microhardness take place. In this case, the effect of sharp increase in microhardness is revealed: its value exceeds the reference quantity (initial one). The possible mechanisms of these phenomena are discussed.

1. Introduction

The interest in studying the interaction of laser radiation with semiconductors arose due to the possibility of modifying and ultimately controlling the properties of both monatomic and more complex systems. The defects arising under irradiation have a significant impact on a number of physical properties (optical, mechanical, etc.), which naturally will affect the stability of operation of devices based on these materials. In this regard, even minor changes in the mechanical properties (microhardness, durability (wear resistance), Young's modulus, etc.) of the material under the action of various external factors become important, and their study is of current concern. In this field of science there are many uninvestigated problems.

One of the manifestations of the interaction of laser irradiation pulse with a solid is the generation of a powerful pulse of compression. It is this region of elastic wave where the most intense generation of defects takes place, which is accompanied by an extreme change in some physical properties [1-5]. These conclusions were clearly confirmed by the experimental data of [3], which evidence that the maximum values of microhardness and dislocation density are observed in the region of the maximum gradient of elastic wave of α-Fe crystals. In addition, the authors of this work found that the maximum microhardness is formed under the surface, at the depth of a significant pressure gradient and the maximum density of dislocations, rather than on the radiation surface.

Similar results were obtained for a number of metals subjected to UV irradiation. It was shown that an increase in microhardness and durability is distributed to a depth of 300 μm; in addition, both an increase and a decrease in the parameters are observed depending on irradiation regime [6]. Moreover, the extreme values of mechanical characteristics do not correspond to the radiation surface of the crystals; they take place at a certain distance from this surface. It was found in [3] that, under irradiation of metal foils by light with $\lambda = 0.95$ μm for 0.2-100 s, the microhardness increases on the radiation surface and on the crystal surface opposite to irradiation. The data clearly show abnormally deep structural changes under laser irradiation. Some possible mechanisms for the abnormally deep changes (for this effect) in structure and microhardness under ionic implantation were proposed [4-7]. Studies of structure change and microhardness modification of Si crystals under ionic bombardment revealed that significant changes in the studied parameters were observed at depths exceeding the distances of ion ranges [5]. The authors assume that similar effects can occur not only under ionic bombardment but also in other cases of energy deposition (laser radiation, ultrasonic treatment, mechanical loading, etc.) when a direct knocking-out of atoms is impossible, and the hindering of particles is due to inelastic (electronic) losses of energy.

The predominated mechanism of light absorption in semiconductors is the electron-hole pair generation when the photon energy exceeds the band gap. The subsequent relaxation of the excited electrons is accompanied by an increase in the intensity of oscillations of the crystal lattice atoms. In this case, the acceleration of impurity rearrangement and defect structure change take place [2].

The literature data presented above show that the modifications of characteristics and evolution of the defect structure of crystals subjected to radiation are interrelated.

However, in the above works, the studies are generally performed immediately after irradiation or the time between irradiation and beginning of the studies was not controlled; that is, the changes that can take place during this time interval (pause) were not taken into account and estimated. Nevertheless, during this time, the self-organization of laser induced defects, which interact with each other, and the so-called room temperature laser annealing can occur. All this causes changes in the strength and other properties of materials treated by laser irradiation.

The regard for changes during annealing will make it possible to refine the laws and mechanisms of changes in properties of materials exposed to pulsed irradiation.

The aim of this work is to study the effect of pulsed laser irradiation and its modes on the mechanical properties of GaP single crystals and to examine the effect of room temperature annealing on radiation effects generated in these crystals.

2. Experimental

We study the effect of pulsed laser irradiation of different power on some parameters characterizing the mechanical properties: microhardness (H), crack sizes around indentations (L), and behavior of dislocations. GaP single crystals, plane (111) were objects of research. Microhardness was measured using a PMT-3 instrument equipped with a Vickers pyramid. The load on indentor was 50g (0.5 N). The measurement error for microhardness was no more than 3%. The method of chemical etching to identify the dislocations was used. The etchant was a boiling solution with the following composition: 6g KOH, 4 g K_3 $Fe(CN)_6$, and 50 ml H_2O. The etching time was 1-2 min. Two irradiation modes were useful: continuous and cycled with pauses between radiation actions. The duration of exposure (irradiation time, t) was varied within 1 to 30 min.

The studies of the effect of annealing (storing at room temperature) were carried out immediately after irradiation and after each stage of storing. The total duration of annealing time after laser action ranged to 40-80 days. We used lasers of pulsed irradiation with following next parameters: laser no. 1: λ = 337.1 nm, f = 50 Hz, t = 15 ns, E = 10 kW/cm^{-2} and laser no. 2: W = 9 MW, f = 10 Hz, t = 10^{-4} s, P = 90 kW, E = 360 kW/cm^{-2}. The power density of laser no. 1 was up to 40 times higher than the power density of laser no. 2.

3. Results and discussion

It was found that modifications of the surface layer microhardness are dependent on laser irradiation power but obtaining the clear correlation between them failed. At certain doses (20-30 minutes of irradiation, laser no. 2) the microhardness magnitude of radiated surface of GaP crystals is increased to 20-30% (Fig. 1).

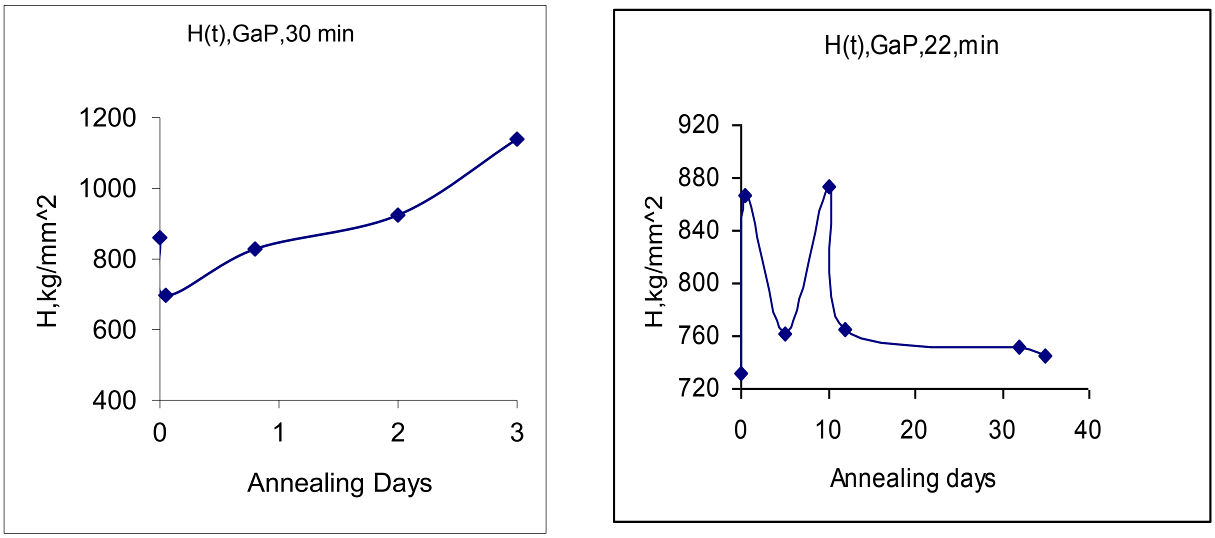


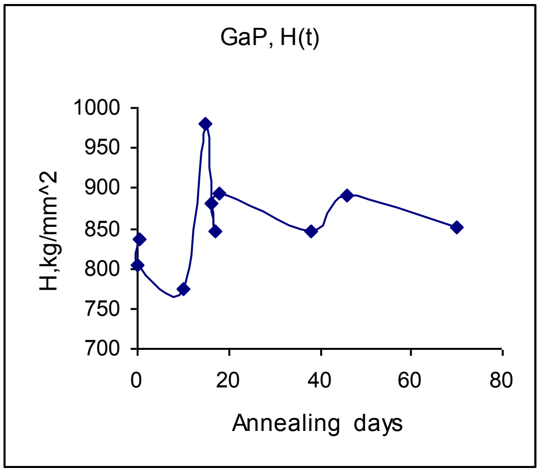
Fig. 1. Dependence of microhardness value on irradiation time (laser no. 2) and subsequent room temperature annealing.

In this case, the microhardness values (Fig. 1, Y-axis) correspond to the nonirradiated and symbolically irradiated samples. This is connected with the X-axis scale.

It is evident from the figure that the degree of increase in microhardness is determined by the radiation dose. The radiation hardening (the increase in microhardness after irradiation) is 30% for the irradiation time of 30 min (Fig. 1a) and 18% for 22 min of radiation (Fig. 1b). The microhardness modification during annealing also varies depending on irradiation dose. A consecutive increase in microhardness is observed after 3 days of annealing (Fig. 1a). The dependence H(t) shown in Fig. 1b at approximately the same stage of annealing (3 days) exhibits another behavior: the hardening gives way to a fairly significant decrease in microhardness. The lower irradiation doses lead to the softening of the GaP crystals (decrease in microhardness) (Fig. 2). We can assume that this is caused by the differences in the microhardness value of the initial samples.

It is evident from the figure that the samples subjected to irradiation for 10 min have approximately the same initial microhardness value. In either case, the radiation softening (decrease in microhardness) was observed and the H(t) dependence during annealing exhibited a similar behavior.

A general feature is the fact that, after the cessation of pulsed radiation laser action, the microhardness continues changing. In both cases, the microhardness change with storage (annealing) time is wave-like: a decrease in the microhardness value is followed by its increase. Note that, during annealing, a region of the maximum increase in microhardness is identified. At the stage of nearly 20 days of annealing, the microhardness is H_{un}=835 kg/mm^2, but the microhardness of the irradiated sample (H_{irr}) exceeds 1000 kg/mm^2 (H_{un} is the microhardness of the initial samples).



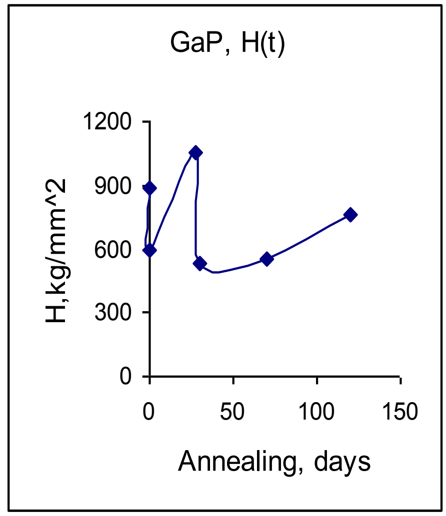


Fig. 2. Dependence of change in the microhardness of GaP single crystals subjected to radiation of lasers no. 2 (a) and no. 1 (b) during the room temperature subsequent annealing.

A certain dependence of change in microhardness upon irradiation and during annealing on the crystallographic direction of indentation was revealed (Fig. 3). On the nonirradiated and irradiated surfaces of the GaP single crystals, indents were made along the certain directions: hard [121] and soft [011]. In this case, the main effect of radiation softening is obtained (Fig. 3). However, it is seen that value of softening is determined by the initial hardness of the direction: the higher the direction hardness, the more significant the decrease in microhardness under laser irradiation. The decrease in microhardness decrease is 13% for [121] direction and 9% for [011]. The experimental data showed that hardness anisotropy inherent in the (111) plane of GaP crystals decreases under the action of laser irradiation. The anisotropy coefficient ($K=H_{max}/H_{min}$) is 1.52 for the nonirradiated crystals and decreases to a value of 1.1 for the irradiated samples. This suggests that pulsed laser irradiation leads to a change not only in separate parameters characterizing mechanical properties, but also in the regularities of these properties of GaP single crystals. The further change in microhardness with increasing time of annealing (aging) exhibits a nonuniform pattern: a decrease in microhardness gives way to its increase and vice versa (Fig. 3).

Note that, at the stage of 30 days of annealing, a significant increase in microhardness was observed (Fig. 3). The effect is similar to that presented in Fig. 2.

It was also found that the joint action of pulsed laser radiation on early activation and subsequent room temperature annealing leads to a decrease not only in the microhardness, but also in the brittleness of the material (Fig. 4). It is evident from Fig. 4b (right indent) or Fig. 4a, within the indents on the untreated surface, the material failures are observed. In contrast, on the irradiated and annealed surface of the GaP crystal, failures are almost absent (Fig. 4c or Fig. 4b, left indent). However, in the last case, the dislocation rows are more intensively formed within the deformed region, and the dislocation density on surface decreases, which is indicative of an increase in the plasticity of the material.

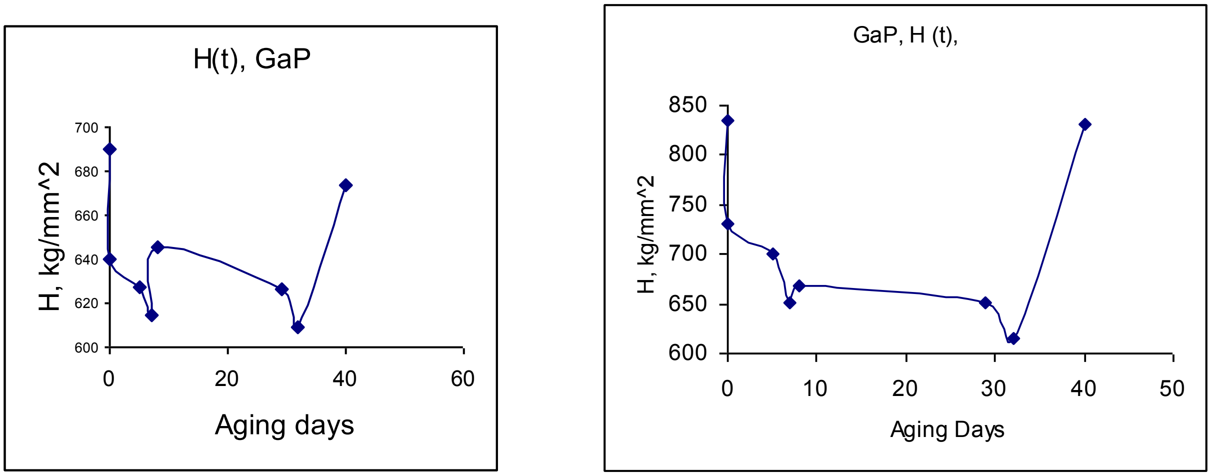
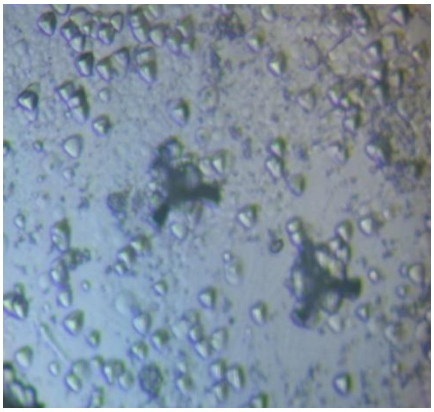
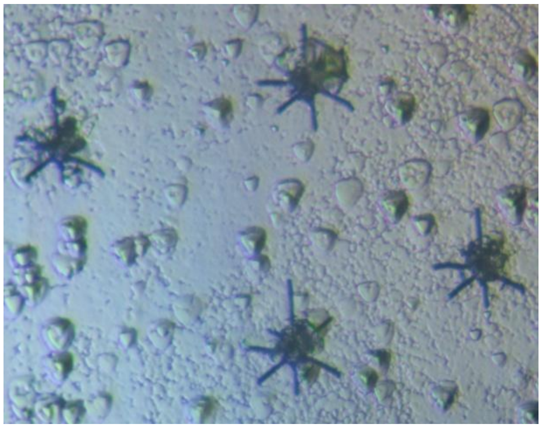


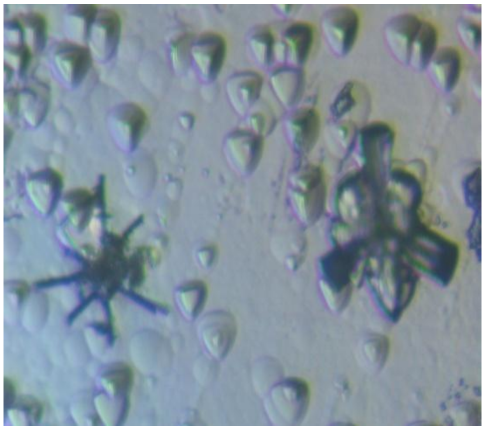
Fig. 3. Dependence of the microhardness of the GaP single crystals subjected to laser radiation (10 min) and the subsequent room temperature annealing. The [121] direction is the hard direction of indentation.



a)



b)



c)

Fig. 4. Image of deformation zone within the indents (P = 50 g) on the (111) plane of the GaP crystals: (a) on the nonirradiated surface, (b) on the surface subjected to irradiation and room temperature annealing, and (c) the right indent on the irradiated surface and the left indent on the nonirradiated and annealed surface. (a), (b) – X600 and (c) – X800.

Table1. Change in the microhardness of nonirradiated and irradiated samples of GaP crystals during room temperature annealing. The time of irradiation is 20 min (laser no. 2).

Room temperature annealing time, days or h	Microhardness value of irradiated crystals, kg/mm^2	Microhardness value of nonirradiated crystals, kg/mm^2
Immediately after irradiation	780±36	814± 20
13 h	836	831
36 h	804	852
days		
10	775	825
15	979 hardening	852
16	973 hardening	800
17	895	834
18	847	834
19	893	857
38	852	857
46	891	-
80	852	854

The data listed in Table 1 give the possibility to confirm the above conclusion: (1) a modification of mechanical properties and hence the structure of the GaP crystals occurs after the cessation of pulsed laser action. This effect can be attributed to the room temperature annealing of the irradiated crystals. (2) At a certain stage of annealing, the microhardness significantly increases and, in some cases, exceeds the microhardness value of the initial nonirradiated sample (Fig. 3, Table 1).

Thus, it was found that, after the cessation of pulsed laser irradiation, the modification of the mechanical properties of the irradiated crystals continues (that means the room temperature annealing) and results in some plasticization of the material and a decrease in dislocation density; at a certain stage of storage, the material hardening takes place (Table 2).

Table 2. Microhardness modification during room temperature annealing of the GaP single crystal, plane (111) subjected to pulsed laser radiation for 20 min. H_{un}= 825 kg/mm^2

Time of storage (annealing) at room temperature, h	Microhardness value, H_a, kg/mm^2	Microhardness change, $\Delta H=H_a- H_{un}$, kg/mm^2
0 immediately after irradiation	874	874-825 = +50 hardening
≥ 20	795	825-795 = -30 softening
36	715	825-715 = -110 softening
70	860	860-825 = +35 hardening
106	959	959-825 = +169 hardening

Thus, analysis of the data suggests that the storage (annealing) of the laser irradiated GaP crystals is followed by an increase in the plasticity of the material. These results are probably connected to the fact that the defect state of the crystal lattice after irradiation is nonequilibrium and convertible. The annealing rather results in this defect state to more equilibrium one and causes a more uniform distribution of impurity defects and residual stresses after pulsed laser irradiation of the GaP crystals. A similar state of defect structure is provided by the recombination processes of the electrons excited by radiation and by the electron-hole pair relaxation. Specified reactions lead to an appropriate modification of the defect structure.

The data of Table 2 show the nonmonotonous pattern of change in the microhardness of the GaP crystal subjected to irradiation and room temperature annealing: the hardening and softening of the material occur.

The experimental results of this work also demonstrate that, under pulsed laser irradiation of the GaP crystals, a similar pattern of change in mechanical properties is observed (Figs. 1-3). The microhardness decreases at small doses of laser radiation and increases at high doses.

Let us to discuss the phenomena observed under the action of pulsed laser radiation on the GaP single crystals. It is known that the action of irradiation action on semiconductors results in the generation of a wide spectrum of point defects (vacancies, interstitials, electron-hole pairs, etc.) with density exceeding the thermodynamic equilibrium. The generation and reformation of defects under excitation of the electron subsystem of nonmetallic crystals is a new type of radiationless transitions in solids which are characterized by large displacements of the atom (several atoms) rather than by heat evolution. The atoms attain additional freedom followed by an increase in their mobility relative to each other and accordingly by a change in the dislocation mobility [8, 9]. In this case, the acceleration of impurity atom redistribution and modification of defect structure took place. Thus, there is a relation of defects generated at electronic subsystem excitation with defects of crystal lattice structure under deformation. An increase in the dislocation mobility stimulates the material softening. However, the effect of point defects on the dislocation mobility causes not only the softening, but also the hardening of the material. The hardening leads to an increase in microhardness. The sign of microhardness modification is rather determined by the degree of occupancy of the electronic state in the subsystem of crystal defect structure. It is obvious that a united consideration of electronic excitements and point defects in solids and their interaction and influence on dislocation mobility present the basis of mechanisms of the hardening or softening effects (increase or decrease in microhardness) in the GaP crystals subjected to pulsed laser irradiation.

It was assumed that dislocation interaction with point defects generated under irradiation also determines the modification of the mechanical properties of crystals subjected to laser radiation during room temperature annealing.

The wave-like pattern of change in microhardness observed during annealing indicated that the state of dislocation-hindering system, its interaction pattern, power and type of hindering play an essential role in this phenomenon [8]. The pattern of change in microhardness suggests the occurrence of two competitive processes during the annealing of the irradiated material.

On the one hand, clusters of vacancies and separate atoms during annealing are scaled down or completely vanish, which stimulates a higher mobility of dislocations introduced during deformation. This leads to a decrease in microhardness. On the other hand, the vacancies as more mobile defects are transferred from clusters to dislocations (sinks of point defects) and inversely hinder the dislocation movement, which means a decrease in microhardness [10]. The sign and value of change in microhardness are determined by the process which is dominant at the stage of investigation.

3. Conclusions

(1) It is found that pulsed laser action (UV region of irradiation) causes an increase or decrease in the microhardbess of the GaP single crystals in dependence on irradiation doze. Small doses of irradiation generally result in the radiation softening (decrease in microhardness). The effect in this case is about 5-6%. For longer action ($t > 30$ min) or

more powerful radiation, the hardening (increase in microhardness) is observed. The radiation hardening in this case is up to 20-30%.

(2) It is revealed that, after the cessation of laser radiation action, the modification of the mechanical properties of the GaP crystals continues.

(3) The changes in microhardness during room temperature annealing are inadequate and exhibit a wave-like behavior: an alternation of increase and decrease in microhardness is observed.

(4) It is found that, at a certain stage of annealing, a sharp increase in microhardness is observed. The microhardness value is higher than that of the initial sample.

(5) An explanation of the observed effects taking into account the dynamics of the excited state of the electronic subsystem of the defect structure is proposed.

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