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THE EFFECT OF HIGH-ENERGY IONS HEAVIER THAN ARGON ON A GERMANIUM SINGLE CRYSTAL AND A NEW MECHANISM OF AUTORECRYSTALLIZATION

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INTRODUCTION

The application of ion beams for semiconductor processing opens up a great variety of possibilities some of which have already been used in practice and some have not been sufficiently developed or verified experimentally. In recent time a growing interest is being shown in high-energy ion implantation /1-4/. The depth layer formed in this process has modified properties and can be used as an absorber of impurities and defects in heat treatment, as well as to create an insulating baffle, a buried interelectrode contact, a vertical field transistor and other elements of 3-dimensional integrated circuits. The recently discovered /5-11/ processes of high-current ion implantation, the ion-stimulated annealing of defects and the annealing of defects by electromagnetic radiation or an electron flux are very important in working out the regimes of ion implantation. So far there are no adequate theoretical descriptions of the defect generation and annealing by nuclear radiations. Some model considerations are discussed in refs. /11-13/. Experimental studies of high energy ($E_L > 0.1\ A_1$ MeV) ion effects on single crystals are promising for a better physical understanding of the processes as well as for progress in technology.

Recently an anomalously low damaging effect of 122 MeV ^{129}Xe ions on a germanium single crystal has been revealed /14/. In going from Ar to Xe the ion damaging power decreases several times. This contradicts known systematics and cannot be explained within the framework of traditional models. A new mechanism has been proposed /14/, of the response of a crystalline medium to energy release along the heavy ion track. This mechanism includes the following stages: transformations of high-density electron excitations to thermal energy, micromelting of medium along the track and the subsequent cooling and recrystallization on the border between the liquid and solid phases. In order to shed some light on the autorecrystallization mechanism of the primary defect volume the measurements of the damaging effect of ions heavier than Ar (with energies of 25-122 MeV) on a Ge single crystal were continued.

1. EXPERIMENTAL

The damaging effect of heavy ions was measured by the crystal blocking technique in the detection of ion elastic scattering products on a Ge single crystal target. The damage control was performed in two variants: "in situ" during the exposure and immediately after the exposure during a short irradiation by the same ions (no differences have been revealed). The Ge substrates used in this work were $(\bar{1}11)$ oriented wafers, 0.1 and 0.2 mm thick, prepared by mechanochemical polishing of the slices from detector quality material (resistivity 10 Ω cm) supplied by "Hoboken-Overpelt". The targets were glued upon the massive metallic element of a goniometric device by a silver paste. Irradiations were carried out at room temperature under nonaligned conditions using external beams from the U-300 cyclotron of the JINR Laboratory of Nuclear Reactions. After passing collimator the beam had the following parameters: an angular spread of $< 0.5°$, a diameter of 1 mm (on target), and an intensity of $\leq 10^{10}$ s^{-1}.

Precipitation of the carbon layer on the target led to a decrease in the yield of the Rutherford scattering products per μC of the beam charge. Thus the layer thickness was controlled and minimized.

Elastically scattered ions and recoil nuclei from Rutherford scattering were recorded using an ordinary glass track detector. The detection threshold of the $Z \geq 10$ nuclei lay at about 5 MeV. The detector was placed at a distance of 120 mm from the target and covered a large scattering angle range, θ_L = 35°-75°. The crystal was oriented so that the <111> axis formed an angle θ_L = 50°-65° with the beam and was directed on to the detector. After the exposure and chemical etching of the tracks a contrast structure of crystallographic reflections in the vicinity of the <111> axis was visually observed on the surface of the glass detector. By scanning the detector and calculating the track density as a function of the coordinate of crossing the reflection one obtains the reflection shape. In the case of the <111> axis of Ge the angular halfwidth of the blocking minimum was found to be $\psi_{1/2} \approx 1.0$-1.3°. Therefore, the role of angular resolution ($\approx 0.2°$) in the detection channel can be neglected. At the beginning of irradiations all the samples exhibited sufficiently intensive blocking minima. The relative particle yield χ_0 measured at the centre of the <111> minimum had values about 0.3-0.4 and a standard statistical deviation of ≈ 0.02.

The observation of the contrast pattern of the blocking effect allows one to watch the crystal damage with increasing heavy ion dose. The number of ions which reached the target during the exposure and fluence value were found from the yield of the detected recoil nuclei and scattered ions based on the known reaction cross section. The determination involves the calculation of the thickness of the

target active layer, d (in beam direction) and the integration of the Rutherford cross section in the ΔE range corresponding to a depth from 0 to d. The range of the bombarding ions is much shorter than the target thickness and the active layer d is considerably smaller than the ion range. The latter circumstance is due to the balance between the energy losses of the incident and detected particles, i.e.

$$k_2 \left\{C_1\left[R_1(E_L) - d\right]\right\}^{n_1} = \left\{C_2\left[R_2(U) + pd\right]\right\}^{n_2}, \qquad (1)$$

where the energy-range relation is approximated by the function $E_i = (C_i R_i)^{n_i}$, the index i = 1 refers to the incident particle; i=2, to the detected particle , E_L is the initial ion energy, U is the detection threshold, k_2 is the ratio between the energies of the reaction product and the projectile, p is the ratio of the pathlength in the target along beam and detection directions. The thickness of the active layer has been calculated by eq. (1) using the particle ranges from ref. /15/, which can give rise to a systematic error of up to 15% in the fluence values obtained. Table 1 gives the d values and other parameters characterizing the experimental conditions.

2. RESULTS

As is known /16/, the blocking effect is unequivocally associated with the geometrical perfection of a crystal lattice. Therefore a decrease in effect intensity with dose gives quantitative information on disorder fraction. In experiments with Ge single crystals the attenuation of the blocking-pattern contrast, the angular spread of reflections, and the extinction of the ordinary axial and planar reflections were observed with increasing fluence. The yield χ_0 at the centre of the blocking minimum is the parameter most sensitive to the lattice damage. Figs. 1 and 2 show the χ_0 values measured for the <111> axis as functions of the fluences of ^{40}Ar, ^{63}Cu, ^{84}Kr, and ^{129,136}Xe ions. In most cases a considerable growth of χ_0 with dose is observed, which indicates a strong damage of the crystal lattice. An exclusion are the bombardments (fig. 2b,c) of germanium by ^{136}Xe ions (116 MeV) and ^{129}Xe ions (122 MeV) in which the conservation of the crystal's good quality is observed up to fluence values of 3×10^{15} cm^{-2}. The anomalously low damaging power of Xe ions (0.9 A_1 MeV) is an unexpected result. Therefore it is necessary to consider the possible trivial explanations, in particular, the thermal annealing of the crystal as a result of its macroheating by the beam.

If the beam with power W is switched on at the initial moment, then the temperature in the region of beam energy release increases

Table 1. Experimental conditions

Projectile	Beam energy, MeV	Beam incidence angle, degrees	Observation angle, degrees	Product energy, MeV		Layer thickness (along the beam), µm		Average beam energy, MeV	Nuclear stopping parameter, (æ), 10^4
				Scattered ion	Recoil nucleus	Scattered ion	Recoil nucleus		
$^{40}Ar^{+2}$	25	60	49	16.1	9.5	1.02	0.56	22	0.83
$^{63}Cu^{+3}$	35	56	53	15.1	12.0	0.94	0.83	31	2.4
$^{84}Kr^{+5}$	73	50	59	9.1	19.3	0.16	0.91	68	2.2
$^{*136}Xe^{+20}$	56	56	53	-	17.6	-	1.31	48	11.5
$^{136}Xe^{+8}$	116	50	59	-	30.0	-	1.43	104	5.4
$^{129}Xe^{+8}$	122	45	64	-	21.6	-	1.20	111	4.8

*The value of the effective ion charge after passage through an absorbing foil is given.

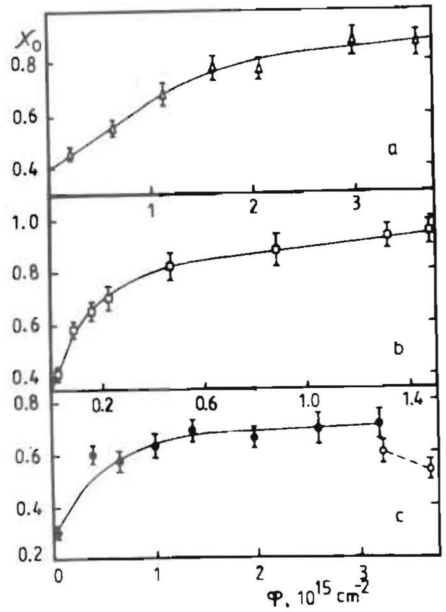

Fig. 1. The yield X_0 in the blocking minimum <111> of Ge, as a function of ion fluence φ: Δ - ^{40}Ar (a), □ - ^{63}Cu (b), • - ^{84}Kr (c), ○ - ^{129}Xe (c)

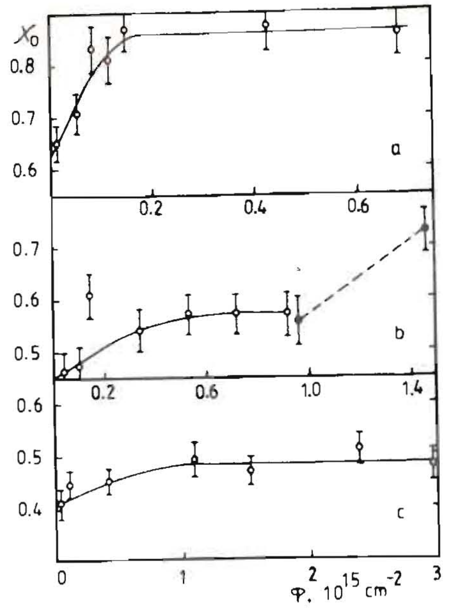

Fig. 2. Same as in fig. 1, for 56 MeV ^{136}Xe (a), 116 MeV ^{136}Xe (b), and 122 MeV ^{129}Xe (c) ions

according to the following law:

$$T = T_0 + \frac{W}{k} \left\langle \frac{x}{S} \right\rangle \left(1 - \exp - \frac{t}{\tau}\right), \qquad (2)$$

where k is the heat conductivity of the material, $\langle x/S \rangle$ is the average ratio of the heat transfer length to the cross section area. The time constant τ is determined by the following equation:

$$\tau = \frac{cV\rho}{k} \left\langle \frac{x}{S} \right\rangle , \qquad (3)$$

where V is the volume of the beam energy release, ρ and c are the density and heat capacitance of the material. The calculation using eqs. (2) and (3) taking into account the pulsed structure of the beam gives an estimate of the equilibrium value of temperature rise $\Delta T \approx 2$-3°C in the case of a ^{129}Xe ion bombardment with a beam intensity of about 5×10^{9} s^{-1} (fig. 2c). The temperature rise is negligibly small compared with the absolute temperature. Experimental verification of the importance of the macrotemperature rise was performed by comparing the results shown in figs. 2b and 2c. In the experiment of fig. 2b the beam intensity was decreased by a factor of 3 and the target thickness was two times smaller compared with fig. 2c. So the temperature rise ΔT was smaller by a factor of 6 while the results changed inconsiderably. Some difference between the data presented in figs. 2b and 2c is due to a change in the detection angle and, correspondingly, to the recoil nuclei energy rather than to ΔT. Therefore, the thermal annealing of defects can be neglected, except the processes occurring at room temperature.

In the present experiments some data about crystal damages by energetic ions heavier than argon were first obtained and the anomaly observed /14/ in going to xenon ions was confirmed. By using the technique of ref. /17/ the measured function $\chi_0(\varphi)$ can be converted to the fluence dependence of the average defect concentration. The result of this conversion for the case of a ^{129}Xe (122 MeV) bombardment is presented in fig. 3. Similar calculations can be carried out for other bombardments but the assumption /17/ concerning the absence of prolonged defects looks unjustified for strong crystal damages. For qualitative considerations it is possible to use directly the dependences $\chi_0(\varphi)$ since the increase of $\chi_0 \to 1$ unambiguously indicates the disorder growth in the target material. Further the damaging power of the ion is characterized in the following way. By extrapolating the dependence $\chi_0(\varphi)$ to $\varphi = 0$ we find the $\chi_0(0)$ value for a non-irradiated crystal and then calculate the extra yield $\chi_{rad}(\varphi)$ in the blocking minimum, due to the radiation dose φ, by the formula

$$\chi_{rad}(\varphi) = 1 - \left[1 - \chi_0(\varphi)\right]\left[1 - \chi_0(0)\right]^{-1}. \qquad (4)$$

After that we determine the dose $\varphi_{0.1}$ corresponding to the value of $\chi_{rad}(\varphi_{0.1}) = 0.1$ and the damaging power of the ion, $\Delta\chi_{rad}/\Delta\varphi = 0.1/\varphi_{0.1}$. This value characterizes the degree of crystal damage per dose unit in an unified way. Now we turn to the discussion of the damaging power of various projectiles.

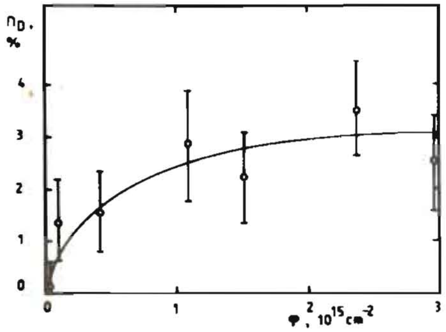

Fig. 3. Defect density as a function of 122 MeV ^{129}Xe ion fluence

3. SYSTEMATICS OF THE DAMAGING POWER VALUES

Nonrelativistic heavy ions produce defects mostly in the elastic scattering on crystal nuclei. The Frenkel pair is formed if the recoil nucleus energy exceeds the threshold value $E_{r.n.} \geq E_{min} \simeq 25$ eV. The multiplicity of defects produced by one displaced nucleus is characterized by the cascade function $\nu(E_{r.n.})$ which is equal to $0.4\,E_{r.n.} \times E_{min}^{-1}$ in the region of $E_{min} \leq E_{r.n.} \leq E_{max}$ and reaches saturation at $E_{r.n.} > E_{max}$. The E_{max} value corresponds to the energy at which nuclear energy losses become considerably lower than electron ones, i.e. reduced energy $\varepsilon_{max} \approx 4$ /18/. By integrating the differential cross section multiplied by the cascade function it is possible to determine the cross section for defect formation, σ_D. If the scattering cross section is assumed to be Rutherford one, then σ_D turns out to be proportional to the coefficient

$$\varkappa = \frac{Z_1^2 Z_2^2 A_1}{\varepsilon_L A_2} . \qquad (5)$$

In order to specify the σ_D values the screened differential cross section was taken according to formulas from ref. /19/ in the scattering angle range between θ_{min} and θ_{max} (corresponding to $E_{r.n.} = E_{min}$ and E_{max}).

At $\theta > \theta_{max}$ the Rutherford cross section was employed. As a result, the following expression was obtained

$$\sigma_D(cm^2) = \frac{3.62\,10^{-13} a\, Z_1 Z_2 \sqrt{A_1}}{\sqrt{A_2 E_L}\;\; E_{min}} \int_{\theta_{min}}^{\theta_{max}} f(t^{1/2})\, d\theta \; + \; \frac{2.60\,10^{-26} Z_1^2 Z_2^2 A_1}{A_2 E_L\, E_{min}} , \qquad (6)$$

where a is the Thomas-Fermi screening parameter, the universal scattering function $f(t^{1/2})$ was proposed in ref. /18/ and numerically formulated in ref./19/, $t = \varepsilon^2 \sin^2\theta/2$, and ε is the reduced energy of the incident particle:

$$\varepsilon = a A_2 E_L \left[e^2 Z_1^2 Z_2^2 (A_1 + A_2)\right]^{-1} .$$

The numerical calculation according to the corresponding program gives the σ_D values which are much smaller than those obtained using the Rutherford cross section. At the same time, the ratios of σ_D are sufficiently close to those of the coefficient $\varkappa$ for different projectiles. This fact makes it possible to use the $\varkappa$ value as a parameter for damaging power systematization. Earlier the proportionality of the ion damaging power to the coefficient $\varkappa$ was observed in ref./3/ for a GaP single crystal bombarded by energetic ions ranging from ^{1}H to ^{40}Ar. A similar dependence was also obtained /20/ for a Ge single crystal bombarded by ions lighter than Ar. The measurements described in the present paper allow one to advance to the region of the heavier ions up to $Z_1 = 54$. The ion damaging power $\Delta \mathcal{X}_{rad}/\Delta \Phi$ versus $\varkappa$ plot is shown in fig. 4. It is seen that the majority of the points lie on a linear dependence. However, the results for Xe ions with an energy of $0.9 \cdot A_1$ MeV do not correspond to the systematics. This corroborates the conclusion /14/ that a new mechanism of crystal response to its primary damage is switched on.

Experimental results shed some light on the details of the new response mechanism. If its origin is due to high energy release, then the ion stopping power dE/dx should be a natural parameter. It is of help to plot the ion damaging power versus $(dE/dx)_{electron}$ as shown in fig. 5. All the points on this figure including those relevant to Xe lie on a common regular dependence with a maximum. An initial growth is due to an increase in $\varkappa$ and the decrease corresponds to a sharp departure from systematics (fig. 4).

From the data presented in fig. 5 it is easy to reveal the threshold activation of the new response mechanism for $(dE/dx)_{electron} > 23$ MeV cm^2/mg. This evidence confirms the type of mechanism associated with thermal microprocesses in the region of the track of a highly ionizing particle. The mechanisms of different nature, as in, e.g., refs. /11-13/, are uncapable of accounting for threshold activation for ions with a high stopping power.

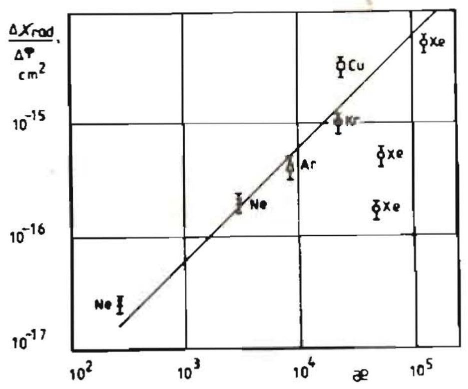

Fig. 4. Correlation between the ion damaging power and the nuclear energy loss parameter

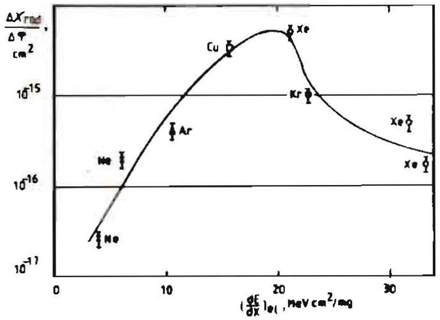

Fig. 5. Ion damaging power as a function of the electron stopping power

4. DISCUSSION

The presently known processes of high-current ion implantation /5-7/ and ion-stimulated annealing of defects (e.g. refs./8,11/) have common features, in particular the crystals are subjected to the effects of the ion beam and macroscopic heating simultaneously. In addition, in all cases the influence of the subsequent irradiation on the earlier produced defects takes place. The autorecrystallization we have revealed in the region of primary damage is different from known processes /5-13/. To say nothing of the different ranges of the energy and ion-Z_1 the actual difference lies in the fact that macroscopic heating of the beam irradiated volume is eliminated in our experiments and the damage maximum /5-7/ depending on the dose has not been observed.

Nevertheless one can see here nothing more than Xe stimulated annealing of the primary defects by subsequent ions. But this explanation should be rejected because the fact why 120 MeV Xe ions are efficient for annealing while 50 MeV Xe and other ions are not cannot be understood. A difference from known processes is evident since annealing stimulated by ^{4}He and ^{75}As ions has been observed /8,11/ successively under the conditions of crystal heating. Thus, the observation of the anomalously low damaging power of Xe ions ($0.9 \cdot A_1$ MeV) at room temperature cannot be explained by known mechanisms. It remains to admit that autorecrystallization occurs as a result of thermal processes in the region of the highly ionizing particle track.

The new mechanism cannot be termed annealing since in this case the self-restoration of each track region rather than the effect of one track on others takes place. However, if micromelting and recrystallization occur they can be employed to restore (anneal) the previously damaged crystals by a Xe ion beam ($0.9 \cdot A_1$ MeV). To verify this proposition a series of Kr ion bombardments was followed by two exposures to a Xe beam and vice versa, a series of Xe bombardments ended in Kr exposures. The results obtained are presented in figs. 1c and 2b. It is seen that the crystal damaged by krypton is restored noticeably after being affected by Xe. And vice versa, Kr bombardment causes considerable defect growth in the Xe-irradiated crystal. Consequently the Xe ions ($0.9 \cdot A_1$ MeV) not only do not cause strong damage in the crystal but also are capable of annealing the previously damaged one. These results are in accord with the data intepretation discussed. Attempts to anneal by a 122 MeV ^{129}Xe beam Ge crystals almost completely amorphized by 15 or 44 MeV ^{129}Xe ions proved unsuccessful. As could be expected, epitaxial recrystallization is inefficient in entirely disordered media.

The observation of the strong amorphization of Ge at the Xe ion energy E_L = 15-56 MeV (in contrast to E_L = 116 and 122 MeV) confirms a relationship between the damage degree and $(dE/dx)_{elec}$. It is clear that in the case of implanting very heavy ions at an energy of about 1 MeV/nucleon the surface layer (several μm thick) remains undamaged whereas damage at depth is strong. This type of semiconductor treatment by heavy element implantation may have practical importance.

CONCLUSION

1) By using the crystal blocking technique the damaging effect of Ar, Cu, Kr and Xe ions on a germanium single crystal has been studied at energies in the range of 25-122 MeV. The extremely low

damaging power of 116 and 122 MeV Xe ions has been revealed. It has been established that no anomaly of this kind exists at Xe ion energies $E_L \leq 56$ MeV.

2) A new mechanism of medium response has been proposed which consists in autorecrystallization in the region of primary defects due to micromelting along the track and to epitaxial regrowth.

3) The threshold activation of the new mechanism with increasing ion stopping power has been confirmed experimentally.

4) It has been found that there is a possibility of the high-energy implantation of heavy element ions into semiconductor without damage in the surface layer several μm thick. It is also possible to anneal incompletely amorphized layers in this kind of implantation.

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Воздействие высокоэнергетичных ионов
тяжелее аргона на монокристалл германия
и новый механизм авторекристаллизации

С помощью эффекта теней изучено повреждающее воздействие ионов Ar, Cu, Kr, Xe на монокристалл германия в интервале энергии 25-122 МэВ. Обнаружена аномально низкая повреждающая способность ионов Xe с энергией 116 и 122 МэВ. Предложен новый механизм отклика кристаллической среды на прохождение иона, состоящий в автокристаллизации области первичных повреждений за счет микроплавления вдоль трека и эпитаксиального восстановления. Экспериментально подтверждено пороговое включение нового механизма при увеличении тормозной способности ионов.

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By using the crystal blocking technique the damaging effect of Ar, Cu, Kr, and Xe ions on a Ge single crystal has been studied in the energy range 25-122 MeV. Anomalously low damage is revealed in bombardment with 116 and 122 MeV Xe ions. A new mechanism of crystalline medium response to ion passage is proposed, which consists in autorecrystallization of the region of primary defects due to micromelting along the track and epitaxial regrowth. The threshold activation of the new mechanism, as the stopping power of the ions increases, is confirmed experimentally.

The investigation has been performed at the Laboratory of Nuclear Reactions, JINR.

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