Physical Chemistry

Internal Friction Temperature Spectra in Electron-Irradiated SiGe Alloys


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ABSTRACT. SiGe alloys’ bulk crystals are characterized by prospects of high application in micro- and optoelectronics as a basic semiconductor material. The problem of producing SiGe alloys bulk monocrystals of large diameter has not been solved yet due to the specific difficulties of the crystal growth technology. This concerns the SiGe alloys with high Si or Ge content. Based on the above, a complex investigation of dynamic mechanical characteristics of subsystems of structural defects of SiGe alloys under different external impacts (deformation, radiation, thermal cycling) acquires great importance. Internal friction and shear modulus temperature dependence of the monocrystalline SiGe alloys with Ge up to 3 at % content grown by Czochralski technique is studied in initial and electron irradiated states. Dislocation origin relaxation processes and modulus defects are revealed in a temperature interval of 400-800°C in the internal friction temperature spectra of the initial samples. It is shown that after electron irradiation intensity of relaxation internal friction in the vicinity of 280°C increases and activation parameters of high temperature relaxation processes reveal raising by 10-15%. Electron irradiation causes a decrease in the activation energy values of dislocation origin relaxation processes in the temperature range of 400-800°C. It is opined that these changes might be caused by a decrease in the dislocation mobility in the Cottrell atmosphere enriched by the radiation defects. © 2019 Bull. Georg. Natl. Acad. Sci.

Key words: internal friction, dislocation, radiation defect, thermal annealing

The investigation of defects in SiGe alloys’ bulk crystals was generally carried out by the internal friction method, which is distinguished by high sensitivity to the mechanical stress field formed in the vicinity of crystalline lattice defects. It makes it possible to effectively implement identification of defects of semiconductor SiGe alloys bulk crystals, to establish mechanisms of their influence on the structural sensitive physical-mechanical and electrophysical properties. Such research will help to solve the problem of creating highly efficient semiconductor structures and devices with controllable parameters based on SiGe alloys.

The contribution of a dislocation structure in relaxation and hysteretic processes of torsion oscillations damping in SiGe alloys’ bulk crystals
has been studied [1-3]. Decrease of the activation characteristics of relaxation processes of dislocation origin is shown by influence of a relatively small content of Ge (1-3 at %). Reduction by ~15% in the microplastic deformation characteristics has been revealed at 600-650°C temperatures in Si1-xGex (x≤0.02) alloys containing dislocations of 10⁴-10⁵ cm⁻² densities [1]. An additional reduction of internal friction activation characteristics has been revealed in Si1-xGex (x≤0.01) alloys doped with As or B of 10¹⁸-10²⁰ cm⁻³ concentration [4]. SiGe alloys are characterized by different types of dislocations with distinctly different energetic and dynamic parameters [5-7]. This conditions the formation of complex internal friction spectra related to the motion of dislocations.

Relaxation maximum with activation energy ~1.4 eV was revealed at 280°C temperature at ~1 Hz frequency in internal friction spectrum of p-type monocrystalline Si₀.⁹₈Ge₀.₀₂ irradiated by high energetic electrons of fluence ~10¹³ cm⁻². Its relation to the radiation-induced vacancy-oxygen complexes is supposed [3].

SiGe bulk crystals were grown by the Czochralski method in argon atmosphere. Seeds of Si single crystal with (111) orientation were used for the growth of the SiGe crystals. Microstructure was investigated on the optical microscope NMM-80RF/TRF. Electrophysical characteristics were determined in the constant magnetic field of 0.5 Tesla induction on the Ecopia HMS-3000 device by Hall effect measurements.

Optical absorption spectra in the range of 3-28μm of IR irradiation were studied on Cary 660 FTIR Spectrometer. Investigations of temperature dependent internal friction and shear modulus were carried out on the vacuum device by registration of logarithmic decrement of damping and frequency of free torsion oscillations in the ranges of 20-800°C temperature and 0.5-5.0 Hz frequency. The measurements were conducted at 2°C/min heating velocity.

SiGe samples of [111] orientation and 0.8x0.8x(30-35) mm³ sizes were used for investigating dynamic mechanical properties. Other researches were carried out on the mechanical double-polished 500 μm thickness plates of (111) orientation.

The activation energy of relaxation internal friction maxima was determined by the formula [8]:

\[
H = R \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \ln \left( \frac{f_2}{f_1} \right),
\]

where \( R \) is gas constant, \( T_1, T_2 \) are temperatures of maxima at \( f_1 \) and \( f_2 \) frequencies.

The values of frequency factor \( \frac{1}{\tau_0} \) were determined from the known equation \( \omega_0 \cdot \tau = 1 \), where \( \omega_0 \) is angular frequency of the motion of dislocations, \( \tau \) is relaxation time, and \( R, T \) are temperature and thermal energy of the system.

Microstructure of Si, Si₀.⁹₉Ge₀.₀⁰₅, Si₀.⁹₈₉Ge₀.₀₁₂ and Si₀.₉₉₇Ge₀.₀₃ alloys on the (111) planes is characterized by a non-uniform distribution of dislocation etch pits. Dislocation groups are often fixed in the microstructure of Si₀.₉₉₇Ge₀.₀₃ alloys.

<table>
<thead>
<tr>
<th>Experimental Samples</th>
<th>Dislocation density, cm⁻²</th>
<th>Current carriers concentration, cm⁻³</th>
<th>Current carriers mobility, cm²v⁻¹s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial</td>
<td>Electron-irradiated</td>
<td>Annealed at 300°C, 1 h.</td>
</tr>
<tr>
<td>Si</td>
<td>2 10⁴</td>
<td>7 10¹³</td>
<td>1 10¹⁴</td>
</tr>
<tr>
<td>Si₀.⁹₉₉Ge₀.₀⁰₅</td>
<td>5 10⁴</td>
<td>8 10¹³</td>
<td>2 10¹⁴</td>
</tr>
<tr>
<td>Si₀.⁹₈₈Ge₀.₀₁₂</td>
<td>7 10⁴</td>
<td>5 10¹³</td>
<td>5 10¹¹</td>
</tr>
<tr>
<td>Si₀.₉₉₇Ge₀.₀₃</td>
<td>1 10³</td>
<td>5 10¹³</td>
<td>8 10¹³</td>
</tr>
</tbody>
</table>

alloys. The changes of density and distribution of dislocations in the microstructure of the electron-irradiated samples have not been practically revealed. Table 1 shows the dislocation densities revealed in the investigated samples.

All samples in the initial state are characterized by p-type conductivity, low concentration and mobility of current carriers.

Thermal annealing at temperatures of 300-400°C in vacuum does not affect the electrophysical characteristics of non-irradiated Si, Si$_{0.995}$Ge$_{0.005}$ and Si$_{0.988}$Ge$_{0.012}$ samples. Si$_{0.97}$Ge$_{0.03}$ sample in annealed state is characterized by a weak increase of hole mobility. This is conditioned by annihilation of electrically active technological defects distributed in stress fields near the Ge atoms and in the impurity atmosphere around dislocations.

In electron-irradiated samples a significant increase in current carriers’ concentration and their mobility reduction are revealed. Such changes are conditioned by the point defects and their simple complexes formed by irradiation. Thermal annealing of all the samples irradiated with high-energy electrons at 300°C for 1h causes a reduction in the concentration of holes and an increase in the mobility to the initial level. Obviously, the annealing causes transformations in the structure of radiation defects and a reduction in the concentrations of electrically active defects.

Fig. 1 shows IR absorption spectra of the (111) surfaces of Si plates (thickness ~500 µm) in the initial and electron-irradiated states. In both spectra, overlapping maxima are revealed in a wave number range of 500-1500 cm$^{-1}$. Maxima of vacancy-oxygen (VO) and fundamental oscillations of crystalline lattice exist near points of 605 and 1105 cm$^{-1}$. The weak absorption band 885-888 cm$^{-1}$ relates to the neutral charge states of the (VO) defects [9]. In the electron-irradiated Si a new band 2340-2361 cm$^{-1}$ appears. Apart from the above, several traces of the bands of complex composition are revealed in the high frequency area. They may be stipulated by divacancies of different electrical charge states. Thermal annealing at 600°C temperature reduces to a zero the intensity of high-frequency bands in the range of 3000-5500 cm$^{-1}$.

![Fig. 1. IR absorption spectra of monocrystalline Si. 1 – initial state; 2 – after electron irradiation.](image1)

The optical absorption spectrum of Si$_{0.995}$Ge$_{0.005}$ alloy in the initial state is practically identical to the initial spectrum of Si. A weak reduction in the wave number and intensity of clearly expressed maxima is noticeable. In the electron-irradiated state, the traces of absorption bands are more clearly revealed in the high frequency area. The intensity of maxima related to the C and O impurities revealed near 605 and 1106 cm$^{-1}$ respectively decreases. Their decrease is more clearly revealed in Si$_{0.97}$Ge$_{0.03}$ alloy absorption spectrum (Fig. 2). The absorption band of complex composition and intensity is additionally formed in 1200-1400 cm$^{-1}$ interval. The intensity of maxima related to the 885 cm$^{-1}$ band is slightly changed.

![Fig. 2. IR absorption spectra of monocrystalline Si$_{0.97}$Ge$_{0.03}$ alloy. 1 – initial state; 2 – after electron irradiation.](image2)
The IF temperature spectrum $Q^{-1}(T)$ of monocrystalline Si of (111) orientation is characterized by wide maxima in the 100-800°C temperature range (Fig. 3).

Shapes of the IF maxima are distorted by their overlapping and exponentially growing background. The intensity of the IF background and maxima in 400-800°C temperature range significantly increase at high strain amplitudes of $10^{-4}$-$10^{-3}$. This circumstance reveals their dislocation nature.

All IF maxima change their critical temperature by changing oscillations frequency. According to the well-known theory [8], they are of relaxation origin. This is also confirmed by revealing the shear modulus defects being proportional to the maxima intensity (Fig. 4).

### Table 2. Activation characteristics of internal friction relaxation maxima.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Temperature of IF maxima, °C</th>
<th>Activation energy, eV</th>
<th>Frequency factor, s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial state</td>
<td>After electron irradiation</td>
<td>Initial state</td>
</tr>
<tr>
<td>Si</td>
<td>-</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>280</td>
<td>300</td>
<td>1.35</td>
</tr>
<tr>
<td></td>
<td>410</td>
<td>420</td>
<td>1.50</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>615</td>
<td>1.65</td>
</tr>
<tr>
<td></td>
<td>710</td>
<td>725</td>
<td>2.10</td>
</tr>
<tr>
<td>Si$<em>{0.995}$Ge$</em>{0.005}$</td>
<td>100</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>280</td>
<td>300</td>
<td>1.30</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>415</td>
<td>1.60</td>
</tr>
<tr>
<td></td>
<td>590</td>
<td>600</td>
<td>1.70</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>720</td>
<td>2.00</td>
</tr>
<tr>
<td>Si$<em>{0.998}$Ge$</em>{0.012}$</td>
<td>100</td>
<td>100</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>285</td>
<td>285</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>405</td>
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<td></td>
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<td>1.7</td>
</tr>
<tr>
<td></td>
<td>690</td>
<td>700</td>
<td>1.8</td>
</tr>
<tr>
<td>Si$<em>{0.97}$Ge$</em>{0.03}$</td>
<td>100</td>
<td>100</td>
<td>0.90</td>
</tr>
<tr>
<td></td>
<td>280</td>
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<td>1.30</td>
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<tr>
<td></td>
<td>390</td>
<td>400</td>
<td>1.65</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>605</td>
<td>1.65</td>
</tr>
<tr>
<td></td>
<td>685</td>
<td>700</td>
<td>1.90</td>
</tr>
</tbody>
</table>
The values of activation energy and frequency factors are presented in Table 2 [7].

Irradiation of monocrystalline Si by high energy electrons stipulates an increase in the IF intensity at 100 and 280°C and a weak rise in the critical temperatures of relaxation maxima in the 400-800°C temperature range. Electron irradiation of monocrystalline Si causes a rise in the activation characteristics of high-temperature relaxation processes in comparison with identical values of Si in the initial state. Thermal annealing at 600°C for 3 h of electron-irradiated samples of Si completely suppresses the IF maxima at 100 and 280°C temperatures. In the annealed state the IF exponential background shifts towards high temperatures.

The following peculiarities have been revealed in the IF temperature spectra of the monocrystalline SiGe alloys irradiated by high energy electrons (Fig. 5). An increase in the content of Ge stipulates a reduction in the intensity of IF maxima at 100 and 280°C temperatures; however, their activation characteristics remain unchanged in comparison with the identical values in nonirradiated states. The IF maxima revealed in the 400-800°C range are shifting by 15-20°C towards high temperatures. Respectively, an increase in the activation characteristics is clearly shown (Table 2).

Fig. 5. Temperature dependence of internal friction of monocrystalline SiGe alloys after electron irradiation. 1. Si0.995Ge0.005, f0=1.8 Hz; 2. Si0.988Ge0.012, f0=2.0 Hz; 3. Si0.97Ge0.03, f0=2.15 Hz.

Fig. 6 shows temperature changes of shear modulus of electron-irradiated SiGe alloys. At the critical temperatures, the shear modulus defect is revealed in proportion to the relaxation process intensity. Annealing at 600°C for 3 h in vacuum of SiGe samples causes a sharp reduction in the intensity of the IF maxima at 100 and 280°C and a slight decrease in the other maxima intensity. A weak reduction of the shear modulus is revealed at critical temperatures.

Fig. 6. Temperature dependence of shear modulus of monocrystalline SiGe alloys, after electron irradiation. 1. Si0.995Ge0.005, f0=1.8 Hz; 2. Si0.988Ge0.012, f0=2.0 Hz; 3. Si0.97Ge0.03, f0=2.15 Hz.

High-temperature cyclic deformation of SiGe samples at 600°C stipulates a noticeable increase in the relaxation maxima intensity in the 400-800°C range and a reduction in their critical temperatures. Consequently, the shear modulus defects increase at the critical temperatures. It should be noted that activation characteristics of the relaxation maxima at 100 and 280°C temperatures are independent from high-temperature cyclic deformation. Thermal annealing at ≈600°C for 3 h after high-temperature cyclic deformation causes complete suppression of maximum near 100°C and a sharp reduction in the relaxation process intensity in the vicinity of 280°C.

The values of activation energy of 60⁰-edge dislocations motion in SiGe alloys with different content of Ge and Si are determined by studies of mechanical properties [5,7]. Based on the results of both works, it may be supposed that the IF maxima revealed near 400 and 600°C temperatures in the investigated samples are stipulated by moving of
single kinks on 60°-edge and screw dislocations respectively. It may be supposed, that relaxation maximum in the vicinity of 700°C temperature is connected with generation and migration of double-kinks on the 60°- edge dislocations.

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REFERENCES


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