Semiconductor Physics, Quantum Electronics & Optoelectronics, 2005. V. 8, N 3. P. 25-29.

PACS: 62.20.Dc, 81.40.Jj

Low-temperature hysteresis of dynamic shear modulus G_{eff} in silicon

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Abstract. Low-frequency internal friction and dynamic shear modulus (G_{eff}) in Si monocrystal were investigated in the range of 20 to 200 ºC. Temperature hysteresis of internal friction was found and effective shear modulus was studied in the unirradiated and a series of irradiated silicon samples. The appearance of a hysteresis loop is due to interaction of genetic microdefects with crystal point defects and their nonsymmetric distribution in the process of samples heating-cooling.

Keywords: silicon, shear modulus, hysteresis.

Manuscript received 24.06.05; accepted for publication 25.10.05.

1. Introduction

The greatest problem that arises in the course of using semiconductor devices is a change in their parameters with time and due to external factors, such as temperature and hard radiation. The processes occuring in a semiconductor under thermal treatment and irradiation are accompanied by formation of new and interaction of the existing crystal structure defects that mainly affect its photoelectric properties. Any change in photoelectric properties is caused by changes in crystal structure, particularly by changes in defect impurity structure and strain distribution in crystal as a whole [1-4].

Silicon grown by the Czochralsky method has a reasonably complicated system of genetic (hereditary) defects. The absence of dislocations that are effective sinks for point defects (intrinsic and impurity), results in crystals oversaturation with them. Owing to this, in the course of cooling after growing in the dislocation-free silicon monocrystals, various kinds of point defect clusters will be formed. Here belong growth bands and precipitates that resulted from the dissociation of oversaturated solid solutions of background impurities, as well as microdefects of various types (A, B, C, D) [4-6].

Irradiation of semiconductor crystals by high-energy particles results in generation of radiation defects. Due to versatility of secondary processes, the present state of collisions theory prevents from making conclusion on the nature and possible types of radiation defects based on calculations alone [3, 4]. The major role in solving this problem is played by experimental research.

Therefore, the purpose of this paper is to study the processes of formation and diffusion of point defects, growth and decay of microdefects in the process of long-term natural aging of silicon crystals irradiated and unirradiated by high-energy particles.

2. Investigation results

The processes of diffusion, migration, as well as formation of point defect sets will involve changes in the temperature and amplitude spectra of elastic energy and G_{eff} absorption [7-15]. Therefore, to control and study the behaviour of defects (radiation-induced or conventional, growth-induced) in semiconductors [10-15] it is interesting to use the internal friction (IF) method that has been long and successfully used in the investigation of metals [16]. The internal friction method is a resonance technique possessing high structural sensitivity, allowing to determine not only the type, but also the symmetry of defects, their relaxation characteistics, concentration and thermodynamic parameters.

In this paper, the low-frequency IF and dynamic shear modulus G_{eff} in silicon were studied. Silicon monocrystal (*p*-type) grown by the Czochralsky method in direction [111] comprising horizontal and radial growth bands with period of order 150 – 200 μm was chosen as the object of the study. The oxygen concentration, according to IR spectroscopy data, is close to 10^{18} cm^{-3}, boron concentration is about 10^{16} cm^{-3}. Si washers, cut perpendicular to the crystal growth direction, were cut to parallelepipeds 1.5×1.5×60÷80 mm. The samples were subjected to polishing to the depth from 40 to 80 μm and chemical etching to remove the layer damaged on cutting. The direction of applied strain, orientation of faces and the method of samples securing are shown in Fig. 1.

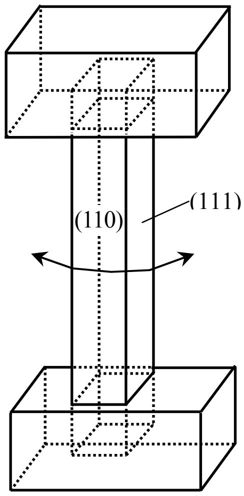

Fig. 1. Orientation of silicon monocrystal faces prepared for investigation by internal friction method and direction of applied alternating-sign strain.

Two groups of samples that were aging at room temperatures for 9 years were studied: the group in the initial state and the group of crystals after irradiation by high-energy electrons of energy 18 MeV, particles flow $\Phi_e = 1.8 \cdot 10^{13}$ el/cm^2 and γ-quanta (irradiation doses made 1.8 and 3.6 kGy for electrons and $4 \cdot 10^4$ rad for γ-quanta, respectively).

IF investigations were performed by torsional oscillations method at frequencies ~2.5 Hz in vacuum ~10^3 Pa at average heating-cooling rate 2–5 degrees per minute, meeting optimal rates of temperature change, when the effects related to point defects in silicon are manifested [8].

Fig. 2 shows the results of studying the elastic energy absorption and dynamic shear modulus in the temperature range of 20 to 200 °C for the unirradiated silicon in the initial state. On the curves of temperature dependence of IF, one can observe a wide weakly differentiated maximum of a complicated nature. Since in these Si crystals linear defects are almost absent, the discovered maximum can be related only to point defects and their sets.

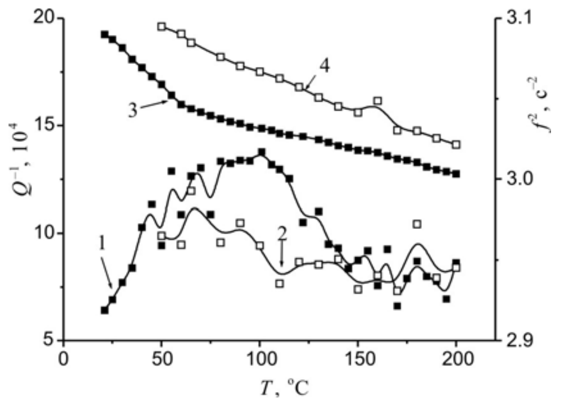

Fig. 2. Temperature dependences of IF (1, 2) and $f^2 \sim G_{\text{eff}}$ (3, 4) of Si. 1, 3 – heating; 2, 4 – cooling.

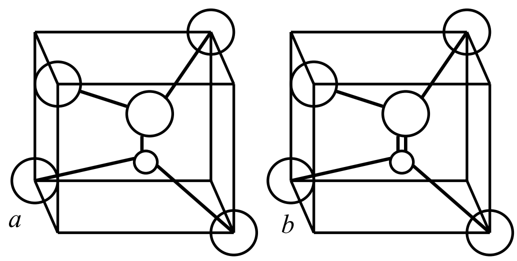

Fig. 3. Defect configuration: a – with neutral boron atom in silicon interstice; b – with negatively charged boron atom forming a double bond to silicon atom.

Maximum energy absorption can be observed only on heating. On cooling, it was essentially smoothed, which testified to its not purely relaxation nature.

Maxima of elastic energy absorption in IF spectra, as a rule, are related to migration of point defects or their sets and originate when the symmetry of field around the point defect or set is lower than lattice symmetry. These defects should include impurities of boron, oxygen, carbon and interstitial silicon. Boron atom, implanted in Si lattice, forms a split interstice with silicon atom – a "dumb-bell", which is asymmetric, since boron atom in it is lighter than the silicon atom [7, 9]. As long as boron in silicon crystal lattice can form several configurations (Fig. 3) with lower than cubic symmetry, each of them can lead to the occurrence of maxima on temperature dependence of IF. The elastic energy absorption is caused by migrations of boron atoms into equivalent positions around the silicon atom. Each such process can be accompanied by maximum absorption with activation energies 0.29 and 0.49 eV. On conversion to frequency 2.5 Hz, we get that IF maxima related to the occurrence of boron must be observed at lower than room temperatures. Thus, the maximum on IF temperature spectrum in Fig. 2 is not related to sets that can be formed by boron in Si lattice [7, 9].

The implanted silicon atom in the nonequivalent positions with a double or single bond (positively charged) can be also considered as a mechanical dipole with lower than lattice symmetry (Fig. 4) [2-5]. This can also result in the appearance of peaks in elastic energy absorption with activation energies 0.7 and 0.92 eV. On conversion to frequency 2.5 Hz, the temperature positions of these maxima will be, respectively, at 13 and 115 °C, actually coinciding with maximum energy absorption in our case. At the same time, a peak caused by reorientation of the silicon mechanical dipole is a relaxation one, that is it should be observed both on heating and cooling and be accompanied by elastic modulus relaxation.

Behaviour of G_{eff} with temperature in Fig. 2 also proves this conclusion, since the presence of relaxation process is not registered. Moreover, on cooling, modulus passes much higher than on heating, which can indicate to considerable structural inhomogeneity of our samples and their different "response" to heating and cooling.

The effective (dynamic) shear modulus can be arbitrarily divided into "lattice" and "deformation" components ($G_{eff} = G_{lat} + G_{def}$). The hysteresis of dynamic elastic modulus can be caused either by a change in G_{lat} during polymorphous transformation (or a different phase precipitation, as mentioned above), or a change in its "deformation" component during the reconstruction of defective structure. Obviously, we are dealing more with a change in the deformation component of dynamic modulus, since, as we know, silicon in this temperature range does not undergo classical temperature polymorphous transformations [11]. The results of amplitude dependences of internal friction of silicon measured at room temperatures and presented in Fig. 5 can serve as a peculiar proof of the above said. A divergence of curves $G_{eff}(\gamma)$ obtained with increasing and decreasing the deformation degree γ, testifies to the increase in G_{def} of silicon during measurement. One of possible reasons for this discrepancy can be the motion of dislocation segments (dislocation bends) and their liberation from impurity atoms due to diffusion.

Analysis of possible behaviour of dislocation-impurity structure under the influence of external periodic force and temperature shows that liberation of dislocation (or dislocation segments) from impurity atoms can really cause the diversity of G_{eff} on heating and cooling, if in the course of measurement the impurity atmosphere has no time to return to the dislocations. As is shown in paper [11] by example of aluminum, the "evaporation-condensation" of impurities from dislocations can bring about the appearance of "direct" hysteresis of dynamic shear modulus: on the temperature dependences of G_{eff} (heating curves pass above cooling curves).

However, in silicon with its high value of the Peierls barrier it is very difficult to shift or at least bend the dislocation, and this can occur at temperatures higher than 600 °C [17]. Though, as shown in Ref. [13], breaking dislocation off the fixing point does not call for reaching critical strain of activation-free overcome of energy barrier, and the motion of dislocation bends in silicon becomes possible even at room temperatures [14]. The bends on dislocations are those places that absorb or emit impurity atoms most easily.

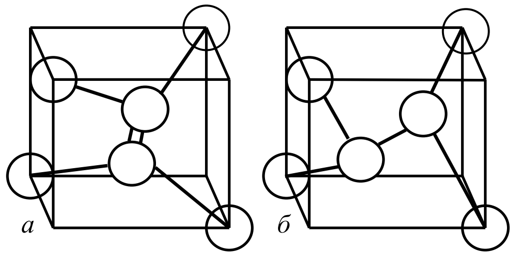

Fig. 4. Defect configuration: a – with neutral interstitial silicon with double bonds, b – with positively charged silicon.

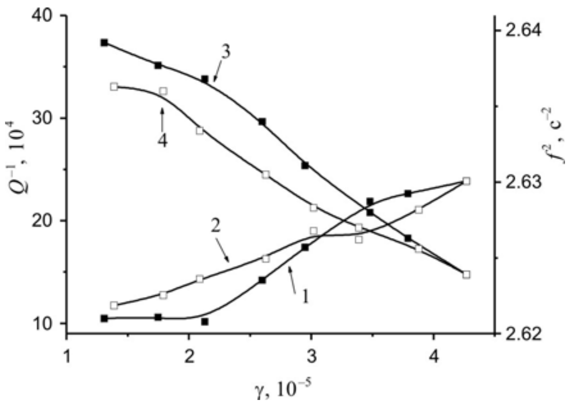

Fig. 5. Amplitude dependences of IF (1, 2) and $f^2 \sim G_{eff}$ (3, 4) of Si with increased deformation amplitude γ (1, 3) and with reduced γ (2, 4).

As a rule, dislocation-free crystals can contain a large number of prismatic dislocation loops (swirl-defects) [2, 4, 6], created due to formation of clusters of excess interstitial atoms on crystal cooling. Cluster formation takes place heterogeneously on some nuclei that include carbon atoms [5].

Crystals under study include a large number of prismatic dislocation loops (swirl-defects). According to accepted classification, these are A-microdefects that are interstitial dislocation loops with the Burgers vector $\vec{b}$ = 1/2 [110], lying in the planes {111} and {110} [2, 4-6]. According to X-ray diffractometry data, their concentration is $n \sim 10^5\,cm^{-3}$, and dimensions $R \sim 5 - 20$ µm [15, 18, 19]. As the temperature increases due to a change in local strains around A-defects and non-uniform distribution of strains in crystal as a whole and under the influence of external alternating-sign strain, the point defects can be redistributed and move either toward the dislocation loop, or away from it depending on the sign of thermal strains and defect type. Probably, with cooling rate chosen, not all the point defects return to their places. This may cause the appearance of temperature hysteresis of effective shear modulus. It is also proved by the fact that hysteresis loop area is narrowed with reduction of cooling rate. At the same time, the hysteresis of modulus G_{eff} may be caused by other reasons, for example, the interaction of oxygen precipitates with applied strains or the growth of oxygen precipitates or their decay.

Note that silicon annealing at 450 °C which is known to stimulate a decay of oversaturated solid solution of oxygen in silicon, damped temperature hysteresis in the range of 20 to 200 °C, but did not cancel the amplitude one: it became somewhat narrower, but did not disappear (Fig. 6). Narrowing of the amplitude hysteresis is attributable to formation of oxygen precipitates SiO_x, with the field of strains around them blocking the increase or reduction of dimensions "motion" of A-microdefects.

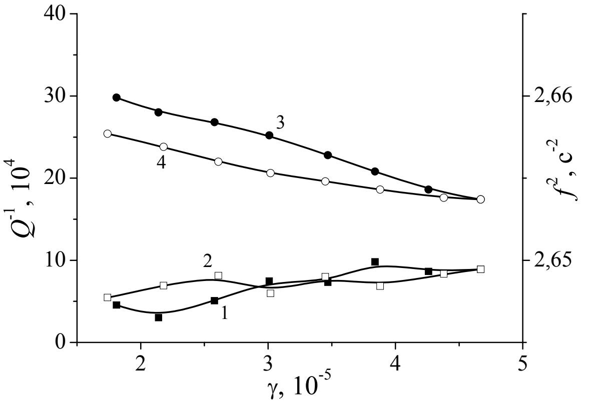

Fig. 6. Amplitude dependences of IF (1, 2) and f^2(3, 4) of Si on holding at 450 °C for 5 hours. 1, 3 – with increasing *γ*, 2, 4 – with reducing γ.

Fig. 7 shows the curves of the temperature dependence of internal friction and the effective shear modulus in silicon after irradiation with the electron dose 3.6 kGy and gamma-quanta. The irradiation initiated the disappearance of IF maximum in the region of 100 °C and temperature hysteresis of the elastic modulus. The behaviour of G_{eff} with temperature indicates that the sample structure has become more homogeneous. For the majority of samples the IF becomes more stable.

So, in the course of long-term silicon aging, IF maximum and shear modulus hysteresis in the range of 20 to 200 ºC is probably caused by the interaction of microdefects with point defects. Irradiation by high-energy particles blocks the "motion" of these microdefects. Dissociation of oversaturated solid solution of oxygen in silicon and formation of SiO_x precipitates also restricts considerably such defects – the elastic modulus hysteresis in the range of 20 to 200 ºC disappears.

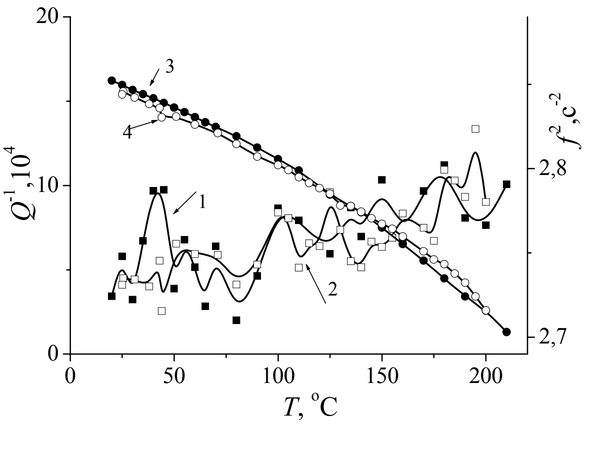

Fig. 7. Temperature dependences of internal friction (1, 2) and $f^2 \sim G_{eff}$(3, 4) in silicon after irradiation with electrons and gamma-quanta. 1, 3 –heating, 2, 4 – cooling.

Thus, the analysis of temperature spectra of IF combined with X-ray diffractometry data [15, 18, 19] of silicon crystals irradiated with high-energy particles allows making some assumptions as to possible mechanisms and dynamics of structural changes in silicon crystals in the course of long-term natural aging. As long as for Si (Cz) the basic defects are B-type microdefects, under the influence of high-energy irradiation these microdefects may transform into A-type with dimensions ≥ 10 μm.

In so doing, the scheme of possible transformation is as follows [5, 12]:

$(C_sI) + O_i\, I \Rightarrow n[(C_sI) + O_i] \Rightarrow$ B-microdefects;

$B + I_{Si} \Rightarrow$ A-microdefects.

Moreover, one can assume the existence of another type of defects – vacancy sets (*VV*-sets), as long as in mechanical spectra of irradiated silicon (unlike control samples of the first group), under dynamic thermal cycling, maxima in the region of 180 to 220 ºC appear and gain in magnitude. Such defects are typical exactly of *VV*- clusters in silicon planes (111)**.**

3. Conclusions

1. Selective sensitivity of low-frequency internal friction to changes in "genetic defects-point defects" system was discovered.
2. Occurrence of IF hysteresis loop and shear modulus hysteresis in the range of 20 to 200 ºC is related to the interaction between genetic microdefects and point defects in crystal and their nonsymmetric distribution in the course of samples heating-cooling.
3. Irradiation by high-energy particles blocks the increase in dimensions of microdefects. Dissociation of oversaturated solid solution of oxygen in silicon and formation of SiO_x precipitates results in the disappearance of elastic modulus hysteresis in the range of 20 to 200 ºC.
4. In the course of being held at room temperature for nine years, the samples irradiated by high-energy electrons ($E \sim 18$ MeV) with doses 3.6 and 5.4 kGy became more homogeneous in structure as compared to doses 1.8 and 2.7 kGy.

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