Functional Materials 18, No.1 (2011) © 2011 — STC "Institute for Single Crystals"

# Effect of a weak constant magnetic field on the silicon single crystal structure

***V.A.Makara, D.V.Kalinichenko***

T.Schevchenko Kyiv National University,
64 Volodymerska St., 01601 Kyiv, Ukraine

*Received June 23, 2010*

A change in the crystal lattice parameter of *n* type silicon single crystal grown by Czochralski technique under a weak ($B$ ~ 0.2 to 0.4 T) constant magnetic field has been revealed. The effect shows some specific characteristics. First, it has a time-dependent, that is, it disappears after a certain relaxation time, provided that the crystal is not subjected to any subsequent external influences. Second, the lattice parameter was observed to be changed only after influence of a magnetic field exceeding 100 mT. A physical model explaining the effect is proposed. The magnetic field action consists most likely in the transformation of the oxygen-containing clusters (initial or appearing during the growth) in a metastable state where those may be decomposed into their components or simpler defects due to thermal fluctuations.

Методом рентгеновской дифрактометрии выявлено изменение параметра решетки монокристаллического кремния *n*-типа, выращенного методом Чохральского под влиянием слабого ($B$≈0,2–0,4 Т) постоянного магнитного поля. Эффект имеет некоторые характерные черты. Во-первых, он имеет временный характер, т.е. исчезает после определенного времени релаксации, если кристалл дальше не подвергается никаким внешним воздействиям. Во-вторых, изменение параметра решетки наблюдалось только после воздействия магнитным полем больше, чем 100 мТ. Предложена физическая модель наблюдаемого эффекта, в рамках которой объясняется возможность такого влияния слабого магнитного поля на кристаллы. Действие магнитного поля заключается в переводе исходных или ростовых кислородосодержащих кластеров в метастабильное состояние, в котором они могут распадаться под действием термических флуктуаций на составные части или более простые дефекты.

## 1. Introduction

The general properties of semiconductor crystals being used in science and engineering are known to depend on their defect structure and chemical purity both in the surface layer and in the bulk material. The defect formation and the defect structure evolution result in variations in the electrical and other structure-sensitive properties of the crystal. The defect/impurity subsystem, in turn, may undergo substantial transformations due to external factors. The defect subsystem conversion is a rather complex process involving the whole set of impurities, the crystal defects and its treatment prehistory.

Recently, numerous works are published concerning the magnetic field effect on the defect/impurity structure in nonmagnetic materials [1–10]. It is to note, however, that in spite of a large experimental data set, the concepts proposed, and possible physical models, the magnetic field (MF) effect on the real single crystal structure has been not explained physically to date in a complete and unambiguous manner. That is why the studies of novel regularities in that influence will make it possible to develop the novel means to control the defect evolutions in real single crystals as well as to

improve the theoretical model of defect interaction in a crystal.

The possibility of considerable changes in macroscale characteristics of "nonmagnetic" solids (both para- and diamagnets having no ordered magnetic structure) in weak MFs is not quite apparent and is often doubted in spite of numerous publications describing various "magnetic" effects in such materials. So the weak MF effect on different structure-sensitive properties of dielectric crystals (mechanical, electrical, magnetic, surface characteristics) was found in various studies [6, 7, 10, 11]. In those works, numerous concepts and models were proposed for the weak MF effect on the dielectric crystal characteristic changes. Numerous publications are agreed that the effects mentioned are based on the concept of the spin-dependent reactions between the crystal defects that is explained rather well within the spin chemistry theory (see review [12]).

It became obvious in last few years that when considering such effects of weak external factors on a crystal, the elementary atomic interaction acts between all the defect types are to be considered taking into account the charge and spin states thereof to provide a more clear pattern of the internal evolution.

In the previous works [9, 13], the MF effect on micromechanical characteristics of silicon crystals has been revealed, in particular, the microhardness reduction by 20 to 25 % and the corresponding plasticity increase was observed. The revealed microhardness reduction was referred to as the magnetomechanical effect (MME). Taking the above into account, the purpose of this work is to demonstrate the weak constant MF influence on a fundamental crystal characteristic, namely, the crystal lattice parameter, and to reveal the reasons for that influence as far as it is possible.

## 2. Experimental

The phosphorus doped n type conductivity samples of dislocation-free Si single crystals grown by the Czochralski technique and (111)-jriented were used in our experiments. The phosphorus impurity concentration was found to be $1.2\cdot10^{15}$ cm$^{-3}$ using the four probe method. The oxygen content in the silicon crystals was measured by UR spectroscopy and amounted $[O_i] = 1.1\cdot10^{18}$ cm$^{-3}$ in all the samples. The rectangular (20×8) mm$^2$ samples were mechanically and chemically polished at both sides. The samples from different growth batches or from different plates of the same batch were used.

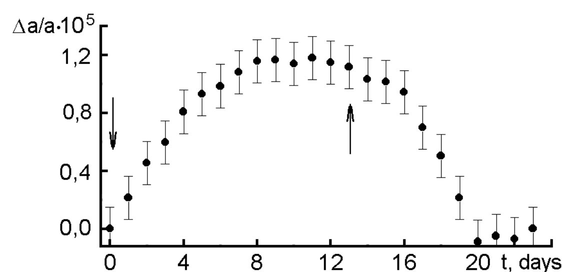


Fig. 1. Dependence of the lattice parameter change $\Delta a/a$ of silicon single crystal on the sample exposure time in MF ($B$ ~ 0.3 T). Arrow downward, the MF action onset, arrow upward, the MF action finish.

The relative change in the crystal lattice parameters measured by three-crystal X-ray diffractometry (TXRD) at room temperature was the main object to be studied in this work. The surrounding temperature was measured to within 0.1°C.

The relative crystal lattice parameters were determined in situ, that is, immediately during the crystal treatment in magnetic field, the crystals were not extracted from the goniometer during the whole experiment after the diffractometer was adjusted. This provided an improved measurement accuracy and a reduced influences of other undesirable factors on the study object. The error of the relative lattice parameter change was about $1.4\cdot10^{-6}$, the Bragg angle for (111) planes $\theta_B \approx 14.28$ deg.

## 3. Results and discussion

To reveal the possible causes of weak constant magnetic field influence on the silicon crystal lattice parameter change, several sample types were studied (n-Si P doped to 4.5 Ohm-cm resistivity, d = 0.45 mm; n-Si P doped to 4.5 Ω·cm resistivity, d = 0.46 mm; n-Si P doped to 2 Ω·cm resistivity, d = 0.5 mm; d being the sample thickness) containing different concentration of dopants and having similar initial parameters, shape, and treatment prehistory. The kinetic dependences $\Delta a(t)/a$ were studied in experiment under different MF induction values acting upon the samples.
All the n-type samples have shown an increase of the lattice parameter (see Fig. 1) as a result of the MF action. The thermal expansion coefficient of silicon single crystal is known to be $\alpha = 2.33\cdot10^{-6}$ K$^{-1}$. The correction to the relative lattice parameter

change associated with the possible change of the crystal temperature by 1 deg was determined as

$$\frac{\Delta a}{a} = \alpha \cdot \Delta T. \quad (1)$$

Fig. 1 shows that the lattice parameter change attains its maximum during 7 or 8 days.

It is to note that the sample removal out of the MF results in the effect relaxation. The MF effect drops substantially to zero during 7 or 8 days. During the subsequent 14 to 20 days, the lattice parameter remained unchanged and corresponded to the data obtained for the initial samples.

Then the lattice parameter change regularities were studied at a constant holding time of a sample in the MF but at different magnetic induction values. The MF exposure time was 7 days for all the samples. These experiments have demonstrated the "threshold" character of the MF action. It is seen in Fig. 2 that the MF induction value causing no lattice parameter change even at long sample exposure time in the MF (up to 10 days) is about 100 mT. To explain that phenomenon, the applied MF can be supposed to result in weakened interatomic bonds and appearing diffuse instability in the crystal according to the singlet-triplet spin conversion [1, 5, 6]. This causes the weakening of all the Si–Si, O–O, Si–O, etc. bonds in the crystal. Due to thermal fluctuations, the growth-induced defect complexes Si–O, V–O, or more complex ones, as $Si_xO_yV_z$, start to decompose. Atomic oxygen and interstitial silicon atoms cause an increased nonequilibrium atomic concentration in the interstices, thus resulting in the impurity concentration gradient and, as a consequence, its diffusion over the crystal. Since the dislocation-free crystals were used, it is just the crystal surface that is the most efficient drain for point defects. But even the plates subjected to all the technological pretreatment stages and chemical/mechanical polishing contain the near-surface microcracks and dislocation half-loops [13]. That layer may be as deep as 5 μm in our case. Those microcracks can be supposed to form the point defect drain channels out of the near-surface layers to the surface.

It is known that each impurity atom causes local stresses of one sign or another in the crystal lattice, thus changing the lattice parameter in a corresponding manner. That dependence is described [14] as

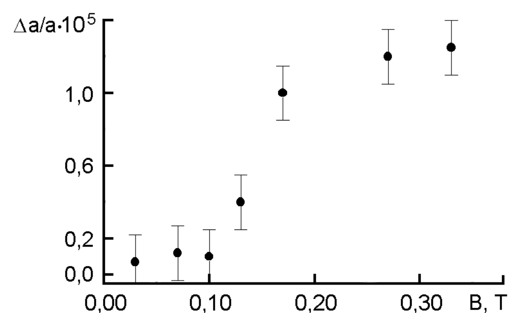


Fig. 2. Dependence of the relative lattice parameter change value of a silicon single crystal on the MF strength. The marks limit the value range obtained for different samples in identical conditions.

$$\frac{\Delta a}{a} = \beta \cdot \Delta C, \quad (2)$$

where β is a coefficient that characterizes the lattice parameter change due to entering single impurity atom (for interstitial oxygen, $\beta = 5.24\cdot10^{-24}$ cm$^3$ [14]); $\Delta C$, the impurity concentration change per unit volume.

Thus, one can say that the MF forms an increased concentration of interstitial oxygen atoms and vacancies. As a result, the concentration of vacancies (acting as the trapping centers of point defects) exceeds considerably the equilibrium concentration for the specified conditions, $N_v > N_{eq}$.

Supposing that the vacancies may act as the adsorbing trapping centers for the atoms moving in the crystal towards its surface, the process can be described in terms of the Langmuir adsorption kinetics. Let $N_v$ be the number of adsorption centers per unit area, then the atom trapping rate by the vacancies can be described as

$$\frac{\partial N}{\partial t} = \eta \cdot (N_v - N) - \gamma \cdot N, \quad (3)$$

where $N_v$ is the number of vacancies; $N$, the number of impurity atoms causing a change in the lattice parameter and the crystal mechanical properties; η, the rate constant of the atom trapping by vacancies; γ, the recombination rate constant. Within a thin subsurface layer, the vacancies are in dynamical equilibrium, that is, the number of forming vacancies is equal to that of disappearing ones due to trapping of an atom, $N_v = const$. Thus, the atomic impurities may migrate from the bulk towards the surface according to interstitial mechanism ($O_i$)

or to vacancy one (V, C, Ph, B). Those impurities may be trapped by the point defect adsorption centers (vacancies).

The solution of Eq. 2 at the entry conditions $N = 0$ at $t = 0$ has the form

$$N = \frac{N_v}{1 + B} \cdot (1 - e^{-At}), \tag{4}$$

where $A = \eta + \gamma$ and $B = \gamma/\eta$. At $\gamma << \eta$, $A = \eta$ and $B <|1$.

When being decomposed into components, the defect complexes cause a change in the lattice parameter; on the other hand, the number of vacancies (acting as the point atom trapping centers) increases. As a result, the equilibrium state is established in the subsurface layer at a certain moment when all the free vacancies diffused to the crystal surface have trapped a fraction of interstitial oxygen and silicon atoms. One can say that the deeper crystal layers become "purified".

Taking into account the supposition that the concentration of impurity atoms influences the lattice parameter change according to Eq.(1), the sample exposure duration in the MF can be supposed to effect its lattice parameter. Then, taking into account the Fick formula

$$X = \sqrt{D \cdot t} \tag{5}$$

the impurity concentration can be supposed to vary along the depth $X$ from the sample surface from the values $C_0 = N_0/X{\cdot}S$ (where $N_0$ is the initial number of the impurity atoms in that layer per 1 cm$^2$ area) down to the values

$$C = \frac{N_0 - N}{X} = \\ = C_0 - \frac{N_v}{(1 + \gamma/\eta) \cdot X} \cdot (1 - e^{-At}) \approx \\ \approx C_0 - \frac{N_v}{\sqrt{D \cdot t}} \cdot (1 - e^{-At}). \tag{6}$$

The expression takes such a value if $\gamma/\eta << 1$, i.e. the trapping rate of interstitial atoms exceeds considerably that of the reverse process in the initial stage. Therefore, one can write for the relative lattice parameter change as a function if the impurity concentration:

$$\frac{\Delta a}{a} = \beta \cdot \frac{N_v}{\sqrt{D \cdot t}} \cdot (1 - e^{-At}). \tag{7}$$

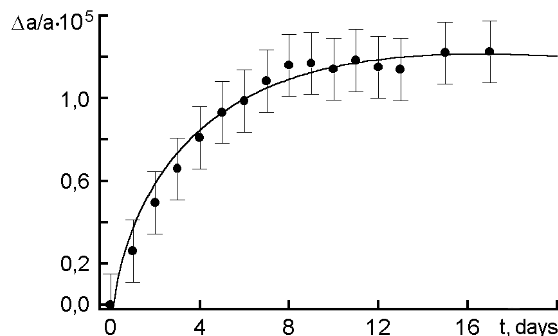


Fig. 3. Kinetics of the relative lattice parameter change value of a silicon single crystal under the MF ($B = 0.27$ T) action. The solid line is the theoretical curve calculated using Eq. 7. The points are the experimental values.

Basing on a series of experiments using the layer-by-layer etching and determination of the diffusion coefficient and the microhardness variations, the following values of parameters were found: $X = 1.15{\cdot}10^{-4}$ cm, $D = 2{\cdot}10^{-21}$ cm$^2$/sec, $N_v = 1.3{\cdot}10^{17}$ cm$^{-2}$, $A = 7.405{\cdot}10^{-2}$ s$^{-1}$.

It is seen from Fig. 3 that the experimental points fit rather well the theoretical curve drawn basing on Eq.(7) using the model concepts.

Thus, the oxygen-containing defects (OCD) are decomposed into a set of point defects due to the MF action. The lattice parameter is influenced most considerably by oxygen with concentrations amounting to $10^{18}$ cm$^{-3}$ in the crystals under study; the concentration of the main electrically active impurity, phosphorus, is as low as $10^{15}$ cm$^{-3}$. The O impurity atoms occupy either interstitials or vacancy-bound positions. The oxygen atoms in interstitial positions are known to stretch the silicon lattice ($\beta = 5.24{\cdot}10^{-24}$ cm$^3$).

It is of importance the lattice parameter increase under the MF shows a correlation vith the reduction in the density and size of the surface nanoaggregates of silicon single crystals (see Fig. 4). The images were obtained using the atomic force microscopy (AFM). The exposure in both weak constant MF and alternating MF results in similar density and size reduction of those surface nanoaggregates. Similar to the lattice parameter, the surface topology relaxes in time to the initial sample characteristics, the number and density of nanoaggregates rises again after a certain holding time of the samples under room conditions.

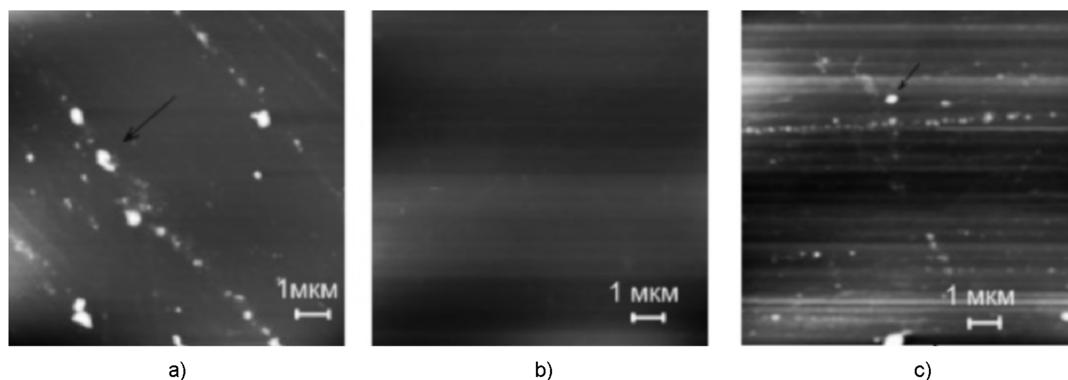


Fig. 4. AFM images of the silicon single crystal surface: a) prior to the MF action; b) immediately after the constant MF action ($B = 0.3$ T, $t = 15$ days); c) after termination of the MF action and the sample holding in air for $t = 5$ days.

Of interest is the fact that the lattice parameter change under MF was not observed in the crystals grown using the zone melting (ZM). This fact confirms that the main contribution to the effect is due to oxygen impurity, since in the ZM crystals the concentration of that impurity is several orders lower than in those grown by the Czochralski technique.

## 5. Conclusions

The effect of a weak constant MF on the lattice parameter change of dislocation-free silicon single crystals grown by the Czochralski technique has been revealed in the work as well as the absence of that effect in ZM grown silicon single crystals. This suggests the decisive part played in the effect by the oxygen impurity. The weak MF influence on the lattice parameter change has been found to be of threshold character. The MF effect on the silicon crystals is shown to be reversible, i.e. to disappear after a certain time, provided the sample is not subjected to any other external influences. The physical interpretation of the MF influence on the changes in the silicon crystal structure properties may be associated with the chemical bond weakening in the crystal and transformation of oxygen-containing structure defects into a metastable state resulting it decomposition thereof into a set of point defects. The concentration change of the latter, in turn, causes a change of the silicon lattice parameter. The MF exposure changes also the silicon crystal surface topology with decomposition of the surface nanoaggregates, that is confermed by AFM images.

## References

1. Yu.I.Golovin, *Fiz. Tverd. Tela*, **46**, 769 (2004).
2. A.M.Orlov, A.A.Skvortsov, L.I.Gonchar, *Fiz. Tverd. Tela*, **43**, 1207 (2001).
3. A.A.Skvortsov, L.I.Gonchar, A.M.Orlov, *Fiz. Tverd. Tela*, **45**, 1603 (2003).
4. Yu.A.Osipyan, R.B.Morgunov, A.A.Baskakov et al., *Pis'ma Zh. Eksp. Teor. Fiz.*, **79**, 158 (2004).
5. R.B.Morgunov, *Usp. Fiz. Nauk*, **174**, 131 (2004).
6. A.M.Orlov, A.A.Skvortsov, A.A.Solovyov, *Fiz. Tverd. Tela*, **45**, 613 (2003).
7. A.A.Skvortsov, A.M.Orlov, V.A.Frolov et al., *Fiz. Tverd. Tela*, **42**, 1814 (2000).
8. V.A.Makara, L.P.Steblenko, N.Ya.Gorid'ko et al., *Fiz. Tverd. Tela*, **43**, 462 (2001).
9. M.N.Levin, B.A.Zon, *Zh. Eksp. Teor. Fiz.*, **111**, 1373 (1997).
10. Yu.I.Golovin, R.B.Morgunov, A.B.Tyutyunnik et al., *Fiz. Tverd. Tela*, **40**, 2184 (1998).
11. Yu.I.Golovin, D.V.Lopatin, R.K.Nikolaev et al., *Fiz. Tverd. Tela*, **48**, 761 (2006).
12. Ya.B.Zeldovich, A.L.Buchachenko, E.L.Frankevich, *Usp. Fiz. Nauk*, **155**, 3 (1988).
13. V.A.Makara, N.N.Novikov, G.N.Nadezhdin et al., *Sverkhtverd. Mater.*, No.4, 57 (1981).
14. V.A.Makara, L.P.Steblenko, N.Ya.Gorid'ko et al., *Ukr. Fiz. Zh.*, **46**, 963 (2001).
15. V.M.Babich, N.I.Bletskan, E.F.Venger, Oxygen in Silicon Single Crystals, Interpress LTD., Kyiv (1997)[in Russian].

# Вплив слабкого постійного магнітного поля на структуру монокристалічного кремнію

***В.А.Макара, Д.В.Калініченко***

Методом рентгенодифрактометрії виявлено зміну параметра гратки монокристалічного кремнію $n$-типу, вирощеного методом Чохральського, під впливом слабкого ($B \approx 0,2-0,4$ Т) постійного магнітного поля. Ефект має деякі характерні відмінності. По-перше, він має тимчасовий характер, тобно зникає після певного часу релаксації, якщо кристал не піддається будь-яким зовнішнім впливам. По-друге, зміна параметра гратки спостерігалася тільки після впливу магнітного поля, яке перевищувало 100 мТ. Запропоновано фізичну модель ефекту, в рамках якої пояснюється можливість такого впливу слабкого магнітного поля на кристали. Вплив магнітного поля полягає у перетворенні початкових або ростових кисневмісних кластерів у метастабільний стан, в якому вони можуть розпадатися на компоненти або простіші дефекти під впливом термічніх флуктуацій.