INVESTIGATION OF CHANGES IN THE X-RAY SCATTERING BY ORDERED DISLOCATION STRUCTURES DURING THE STRAIN AGEING PROCESS

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UDC 539.26; 548.4

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For the first time, we have used triple-crystal X-ray diffractometry for the investigation of the strain ageing of parallel dislocations specially entered into Czochralski-grown silicon samples. The experimental results that testify to a change in the X-ray scattering intensity with ageing are given. Values of the Debye-Waller static factor, sizes, and concentration of X-ray scattering coagulants and changes of these characteristics with the ageing of crystals are determined. The appropriate equal-intensity contours near to (111) node of the reciprocal lattice are constructed. The conclusion about the dislocation-stimulated processes of disintegration of a solid solution of oxygen in silicon is drawn.

1. Introduction

Many authors studied the X-ray scattering by chaotically located dislocations, which are created under growing a monocrystal, experimentally [1] and theoretically [2]. The early experimental researches in this field were carried out on one-crystal diffractometers, whose sensitivity to small changes of the intensity of scattering was insufficient. The authors of later works used two- and even many-crystal diffractometry, which enabled to considerably enhance the possibilities of observations.

Triple-crystal diffractometry has turned out a convenient and high-sensitive method for studies of the structural perfection of semiconductor materials, in particular, which have comparatively small density of defects. Its use, for example, has allowed one even to register the anisotropy of the scattering of X-ray beams, whose reflection plane passes along and across of the row of straight parallel dislocations [3].

It is known that the dislocations as-entered in a crystal during the "strain ageing" process are gradually surrounded by admixture atoms which are present in the material and form the Cottrell "clouds" [4].

The strain ageing of certain crystals was investigated in detail from the viewpoint of its influence on the mobility of dislocations [5, 6]. For semiconductor materials, this process is studied and used as a means to scavenge admixtures from the active zone of a device (the gettering of admixtures) [7]. It is clear that the surrounding of dislocations by Cottrell atmospheres should change the conditions of X-ray diffraction by them. Unfortunately, we do not know the works, in which this question was investigated experimentally or was analyzed theoretically. Therefore, having such a high-sensitivity technique of researches as triple-crystal X-ray diffractometry, we have tried to ascertain the existence of the influence of the strain ageing on X-ray scattering by a dislocation structure. The research of this question is the basic purpose of this work.

2. The Experimental Procedure and Samples

The research was executed on a triple-crystal semiautomatic X-ray diffractometer which worked in the Bragg geometry (n, $-n$, n) under symmetric reflection from surface (111) of Si samples and their turn relative to the Bragg position to the positive side within the angle range from 0 to 220″ with a step of 3—5″. In all events, the constant intensity of the incident Cu$K_{\alpha 1}$ radiation, $I_0 \approx 10^5$ pulse/s, was supported. The diffractometer allowed us to fix the incident point of the X-ray beam on a sample and to automatically register and to reconstruct the diffractograms on a computer monitor with the fixation of the angular positions, integral and peak values of the intensity, and halfwidths of all three diffraction maxima (the diffusion, main, and auxiliary peaks).

The samples were 25×5×0.8 mm in size, cut from the Czochralski-grown dislocationless silicon plates with surface (111) with a concentration of oxygen of about 1×10^{18} cm^{-3}, and made and polished under factory conditions. They were additionally chemically polished with removing a layer of about 20 μm in thickness from their surfaces. According to the method described in [3],

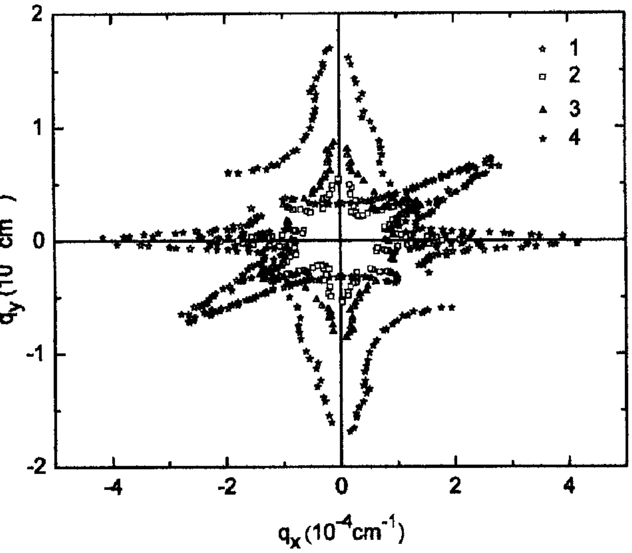

Fig. 1. Contours of equal intensity (44 pulse/s) near (111) node of the reciprocal lattice of silicon: *1* — reference sample; *2* — sample which exposed to ageing during 0 minutes; *3* — sample which exposed to ageing during 15; *4* — sample which exposed to ageing during 40

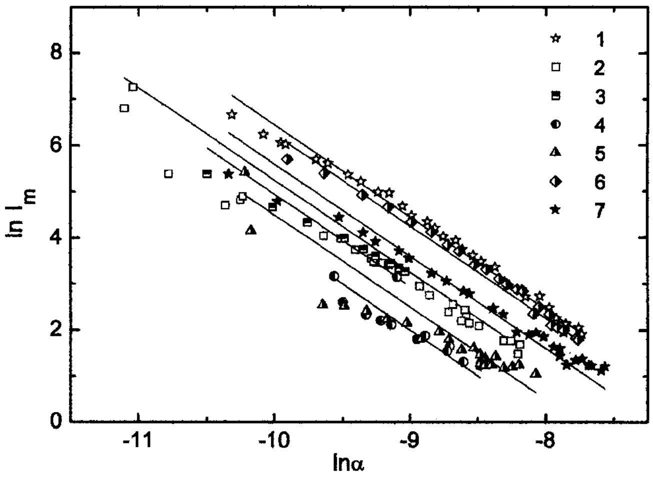

Fig. 2. Dependences lnI_m — lnα for reference samples (*1*) and those exposed to ageing during 3 minutes (*3*), 5 (*4*), 15 (*5*), 25 (*6*), 40 (*7*)

we entered the parallel dislocations lying in planes ($1\bar{1}1$) into the samples and moved the dislocations away from a scratch at a temperature of 600 °C and a pressure of 14 MPa. Their density was fixed and was about 10^5 cm^{-2}. Unlike [3], after the introduction of dislocations, the pressure was removed, and the samples were held at the same temperature 600 °C for a certain time t_{ag}, during which the strain ageing of dislocations occurred. Then a stove was switched off, and the sample being at a pressure was cooled down to room temperature approximately for 1 h. After annealing, the sample was washed in hydrofluoric acid to remove the oxide layer from the surface. As is well known, the main admixtures, which actively interact with dislocations in silicon, are oxygen and nitrogen [8, 9]. The concentration of nitrogen in Czochralski-grown silicon is 10^3 times smaller than that of oxygen. So we hoped that the process of ageing must be mainly conditioned by the movement of oxygen atoms.

3. Experimental Data and Their Discussion

Diffractograms were got from the samples which were subjected to ageing during 0, 3, 5, 15, 25, and 40 min. They also were compared with the diffractograms derived from a reference sample cut from the same ingot of silicon, into which no dislocations were introduced. From each sample, we got approximately 40 diffractograms with turn angles from 0 up to 100$''$. Diffractograms had a usual three-peak view with various intensities of the peaks depending on the previous treatment of a sample. On the reference crystal, the diffusion peak was not practically observed due to its small intensity as compared to the potentiality of its registration by our device. The derived diffractograms allowed us to construct equal-intensity contours near point (111) of the reciprocal lattice with the use of a technique described in [16]. They are given in Fig. 1. It is well seen that, with increase in the ageing time, the intensity of the diffusion scattering peak sharply increases. The diffusion peak overlaps gradually the coherent area which decreases in size and snuggles to the reciprocal lattice point.

In [10], it was shown theoretically that, with fixed $\alpha \geq \beta$ (where β is the peak half-width), the intensities of the main peaks of diffractograms are directly related to the Debye—Waller static factor of samples. Namely, $I_1/I_2 = e^{-2L_1}/e^{-2L_2}$ and $I \sim \alpha^{-2}$. So the comparison of the intensities of the main peaks of a sample I and the standard I_0 enables us to find the static factor of the sample material if a value L for the standard is known. Our standard had $L_0 \approx (2 \div 3) \times 10^{-3}$. That is, $E = e^{-L_0}$ was approximately equal to 1 for it. Therefore, with α =const, we have $I/I_0 \approx e^{-2L}$, which enables us to easily calculate L of samples.

In Fig. 2, the dependences $I(\alpha)$ for all investigated samples are given. It is clear that the plots ln$I$ ∼lnα have a slope of about 2, as was foreseen theoretically. The usage of this dependence for $\alpha = 30''$ enables us to

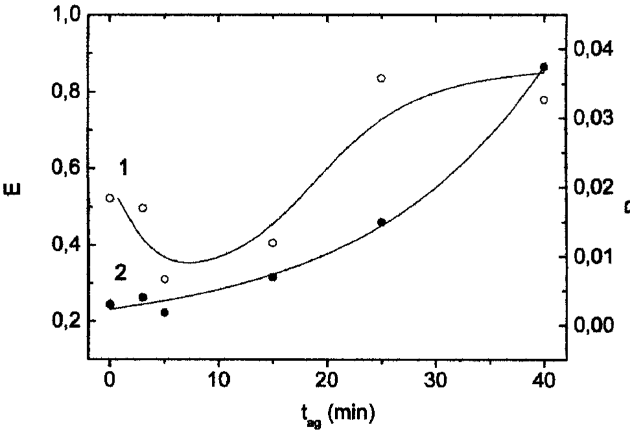

Fig. 3. Change depending on ageing time a material of the parameter E (*1*) and the integrated intensity of the diffuse peak (*2*)

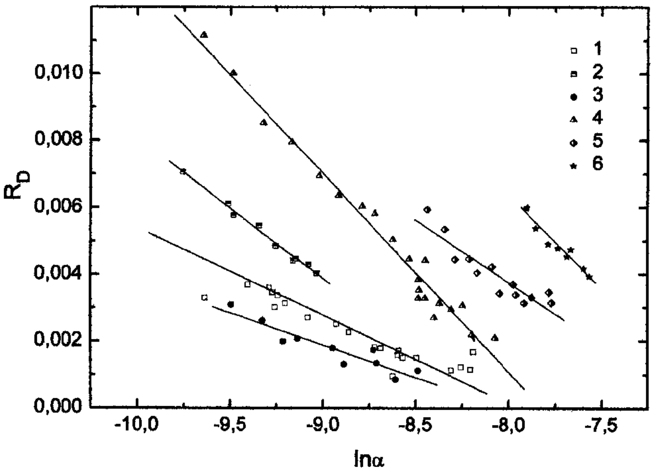

Fig. 4. Dependence R_D on lnα for samples which exposed to ageing during 3 minutes (*2*), 5 (*3*), 15 (*4*), 25 (*5*), 40 (*6*)

determine changes of the parameter L depending on the ageing time of a material (Fig. 3). As seen, its value increases firstly with the ageing time and then begins to decrease. It is necessary to pay attention to significant values of the derived L. It is known [2] that this parameter is directly related to the density of dislocations and is $L \approx \frac{\pi}{6}\rho(Hb\Lambda/4\pi)^2$ for their chaotic location, where H is a vector of the reciprocal lattice, b is the Burgers vector, Λ is the extinction length, and ρ is the density of dislocations. For the dislocation density to be less than $10^5 \div 10^6$cm^{-2}, the value of L should not exceed one-two tenths, which is several times less than the value observed experimentally. The reason for such a difference can be, on the one hand, the ordered arrangement of dislocations, which should increase stresses and, hence, the mean square deviation of atoms from the equilibrium positions and, on the other hand, the surrounding of dislocations by Cottrell atmospheres, i.e. by areas with the increased concentration of admixtures and hence, with the greater probability of their coagulation. It is known that the dislocations are surrounded by atmospheres at the first stages of the strain ageing. Further, when the concentration of admixtures attains a certain critical value, they coagulate by forming the cluster centers (thresholds, kinks, etc.) for the pinning of dislocations in the irregular regions of their location [6, 8, 9, 11].

The clustering of admixtures causes the origination of the powerful diffusion scattering, the study of which enables one to estimate the sizes and concentration of precipitates. Certainly, these processes in Czochralski-grown silicon occur in the temperature interval 600—1100 °C [12] and become visible with the use of X-ray diffraction analysis at the sufficient concentration and sizes of precipitates, which takes place upon a long-term annealing of samples in the temperature interval 800—1100 °C [13].

Since the disintegration of a solid solution of oxygen can be accelerated in stressed crystal areas oversaturated by oxygen, the integrated intensity of the diffuse peak becomes significant already under short-term annealing of researched samples at the temperature 600 °C (Fig. 3). As is known [14], the integrated intensity of the diffuse peak R_D with the not so large sizes of scattering centers is defined by a ratio:

$$R_D = \frac{cC^2E^2m_0 j(K_0)}{2\mu}. \quad (1)$$

Here, c — concentration of scattering centers, μ – linear coefficient of photovoltaic absorption, m_0 is a constant equal to 0.169 cm^{-1} for (111) reflections of silicon, C is the polarization multiplier, and $j(K_0)$ is a complicated function which is defined as

$$j(K_0) = B_K(2.081 \times 10^{14} R_0^2\alpha^2 - \ln R_0\alpha - 17.183) \quad (2)$$

for the small cluster sizes R_0 and for medium turn angles of the sample α. Here, the value of B_K averaged for flat and spherical clusters is equal to $3.59\times10^{39}R_0^{5.4}$ [13].

In all these expressions, R_0 is taken in centimeters, and α in radians.

For small $R_0\alpha$, the first term in the parentheses in (2) can be neglected, and then the dependence R_D on lnα should be linear. Such a dependence is really observed experimentally (Fig. 4) for not very large α. It is clear that the extrapolation of the derived straight lines to the crossing with the abscissa ($R_D = 0$) enables us to

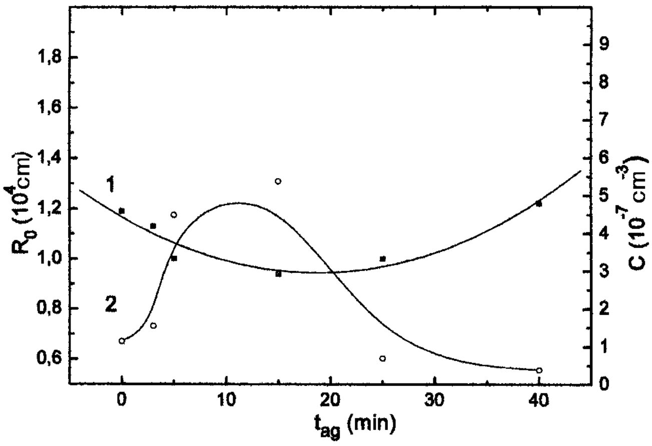

Fig. 5. Dependences R_0 (*1*) and c (*2*) on ageing time

directly estimate R_0. Their values depending on the ageing time of samples are shown in Fig. 5. A small decrease in the sizes of scattering centers for the ageing time of 10 min and their further increase are clearly visible. Such a behavior of the curve can be related to the running of two competing processes: the gathering of admixture atoms in the atmospheres and their flow over the dislocation cores into coagulation centers.

In [15], the Debye—Waller static factor was associated to the sizes of scattering centers and their concentration:

$$L = cn_0\eta^{3/2}, \qquad (3)$$

where $n_0 = \frac{4}{3}\pi R_0^3/v_c$, $\eta = \alpha_0\eta^{1/3}h$, $h = \frac{|H|a}{2\pi}$, $v_c = a^3/8$, a is the lattice constant, $|H|$ is the modulus of a vector of the reciprocal lattice, and the constant $\alpha_0 \approx 3.33\times10^{-2}$ for silicon.

Formula (3) is valid for $\eta^2 \gg 10$, which is satisfied for our sizes of clusters ($\eta \approx 340$). So, by using (3) and neglecting the purely dislocation contribution to L, we can find the concentration of clusters. The derived dependence of the concentration of clusters on the ageing time is given in Fig. 5 and is in agreement with the above-stated suggestions about the existence of two competing processes: the formation of the admixture atmospheres and the flow of atoms from the atmospheres to coagulation centers. First, the number of coagulation centers grows with time, and afterwards, as it always happens during the processes of disintegration and coagulation, their total concentration decreases at the expense of the disappearance of small centers. By these data, it is difficult to estimate the distance between coagulants on a dislocation. With the concentration of dislocations of the order of 10^4 cm^{-2} and the concentration of coagulants of about 10^7 cm^{-3}, this distance should be a few tens of micrometers on the average. It is known that the distance between the so-called "strong obstacles" dividing dislocations into pieces which move as the whole has the same order of magnitude [5].

4. Conclusions

1. We have carried out the study of changes of the intensity of the scattering of X-ray beams in the process of strain ageing of the parallel dislocations as-doped in Czochralski-grown Si monocrystals for the first time.

2. It is established that the process of disintegration of a solid solution of oxygen is accelerated in relation to dislocationless samples in such crystals, and the formation of X-ray scattering centers can be observed already at 600 ^{0}C with the holding of samples at this temperature for at most 1 h.

3. In this case, triple-crystal diffractometry enables us to observe a decrease of the coherent scattering intensity and an increase of the diffusion scattering intensity. The latter is related, as the authors guess, to the clusterization of disintegration products of a solid solution of oxygen on dislocations or near them. The comparison of the experimental data to the theory enables us to estimate the sizes and concentration of formed clusters. The derived data testify to that the clusterization is probably divided into two stages. During the strain ageing of samples, the small groups of X-ray scattering centers are formed at the first stage. At the second stage of ageing, the coagulation of already existing X-ray scattering centers with decrease in their concentration and increase in the size takes place.

4. The derived equal-intensity contours near the reciprocal lattice point (111) enable us to speak about an increase of the diffusion scattering intensity during the ageing, which gradually blocks the coherent area. The last is narrowed during the ageing and snuggles to the reciprocal lattice point.

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Received 14.03.05

ДОСЛІДЖЕННЯ ЗМІН РОЗСІЯННЯ РЕНТГЕНІВСЬКИХ ПРОМЕНІВ ВПОРЯДКОВАНИМИ ДИСЛОКАЦІЙНИМИ СТРУКТУРАМИ В ПРОЦЕСІ ДЕФОРМАЦІЙНОГО СТАРІННЯ

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Р е з ю м е

В роботі вперше була використана трикристальна рентгенівська дифрактометрія для вивчення деформаційного старіння спеціально введених в зразки вирощеного за Чохральським кремнію паралельних дислокацій. Наведено експериментальні результати, що свідчать про зміну інтенсивності розсіяння рентгенівських променів при старінні. Визначено величини статичного фактора Дебая—Валлера, розміри і концентрацію розсіюючих рентгенівське випромінювання коагулянтів і зміни цих характеристик у процесі старіння кристалів. Побудовано відповідні контури однакової інтенсивності поблизу вузла (111) оберненої ґратки. Зроблено висновок про стимулювання дислокаціями процесів розпаду твердого розчину кисню в кремнії.