UDC 669 . 782 : 621 . 38 . 032

Control of Oxygen Precipitation of Epitaxial Wafer by Nitrogen Doping

Katsuhiko NAKAI*1 Koichi KITAHARA*1
Kazunori ISHISAKA*1 Hikaru SAKAMOTO*1
Wataru OHASHI*1

Abstract

Epitaxial wafers have become used as substrates for high integration devices. While they have an advantage of being free from crystal defects on the surface, they have a problem of not having oxygen precipitates working as gettering sites of metallic impurities. By nitrogen doping to accelerate the oxygen precipitation, the authors successfully developed a new epitaxial substrates with a high gettering capacity. Nitrogen-induced oxygen precipitates, several tens of nanometers large, are formed in the nitrogen-doped CZ-Si crystals in as-grown stages and these precipitates grow to be the gettering sites after device processes. It was clarified that precipitate density was determined almost solely by the nitrogen concentration and independent from the temperature and time of the heat treatment, which fact made it easier to control the oxygen precipitation than with the conventional CZ-Si crystals without the nitrogen doping.

1. Introduction

Along with the recent trends of higher integration and finer design rule of silicon devices, demands are increasing for enhanced integrity of single crystals of Czochralski-grown silicon (CZ-Si) used as device substrates. Grown-in defects (void defects: COP[1], dislocation loops[2]) formed during CZ-Si crystals growth have come to be widely discussed, since they cause a decrease in the yield of device manufacturing when they are found on wafer surfaces. Various next-generation technologies have been proposed to make wafers free from the grown-in defects, such as defect-free crystals by special control of growth conditions[3], annealed wafers[4] and epitaxial wafers, etc. Epitaxial wafers have an epitaxial layer on the surface, which is deposited by vapor phase growth and they are free from grown-in defects. (see **Fig. 1**). While this technology is capable of forming a defect-free layer on a wafer surface, it has the drawback that oxygen precipitate density is decreased.

Supersaturated oxygen exists in CZ-Si crystals and it precipitates during an annealing of device manufacturing process, forming oxygen precipitates (A in Fig. 1). When the oxygen precipitates exist in a wafer in an appropriate density, they work as gettering sites to absorb metal contamination, which are inevitably included as contaminants during device processes (intrinsic gettering (IG)). After epitaxial layer growth on a common CZ-Si wafer surface, however, oxygen precipitation nuclei disappears during a high temperature treatment (1,100°C or more) of the epitaxial layer growth process and, thus, the oxygen precipitation does not take place during the device processes thereafter (B in Fig. 1).

As a countermeasure against the insufficient gettering abilities of the epitaxial wafers, a technique called the extrinsic gettering (EG) has been worked out, wherein contaminant metals are collected in a poly-silicon layer grown on the back side of a wafer. As device structure changed and, as a consequence, the process heat treatment

*1 Technical Development Bureau

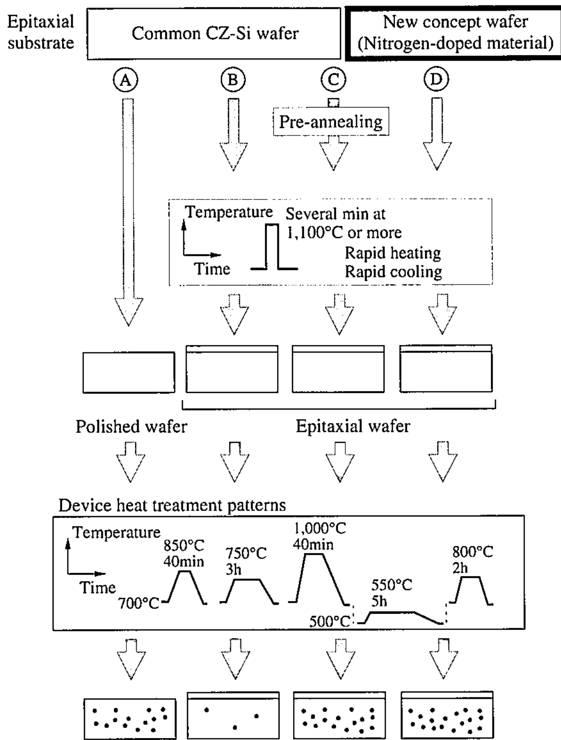

Fig. 1 Manufacturing process of epitaxial wafer and oxygen precipitation after device processes

changed to use lower temperatures for a shorter time, however, it became difficult for the contaminant metals to diffuse to as far as the back side of the wafer thereby hindering the effect of the above gettering sites on the back side. In addition, because double-side polishing will become essential for high flatness wafers to be widely used hereafter such as, typically, 300mm wafers, the EG using the poly-silicon layer will be inappropriate. On the other hand, as a means to enhance the IG capability of the very epitaxial substrates, a method has been studied to secure the oxygen precipitation nuclei, around which the oxygen precipitates form after the epitaxial layer growth, by suitably pre-annealing the wafers before the epitaxial layer growth[5] (C in Fig. 1). This method, however, is costly because of the increased manufacturing steps.

In order to solve the problem, Nippon Steel Group has pursued the possibility to use CZ-Si wafers added with nitrogen as substrates for the epitaxial layer growth (D in Fig. 1), and has succeeded in developing a low-cost, high IG ability epitaxial wafer capable of securing the oxygen precipitates in high density, without involving any additional process steps to cause cost increase (see **Fig. 2**). This

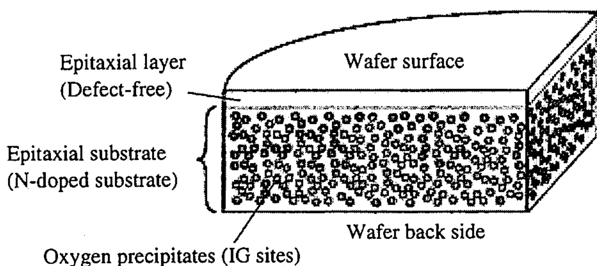

Fig. 2 Schematic sectional view of nitrogen-doped epitaxial wafer

paper reports the precipitation characteristics and metal gettering properties of the epitaxial wafer using a nitrogen-doped substrate (nitrogen-doped epitaxial wafer) developed by the authors. Also discussed is the precipitation mechanism of nitrogen-doped crystals.

2. Experimentation

A 200mm CZ-Si crystals, boron-doped was uses as a dopant and the so-called p^- substrates having a resistivity of 8 to 12 Ωcm and the so-called p^+ substrates having a resistivity of 0.010 to 0.015 Ωcm were prepared. Oxygen concentration of the p^- substrates was measured by Fourier transform infrared spectroscopy (FTIR) from the absorbance of 1,108 cm^{-1}. The value of the conversion factor used here was $3.03 \times 10^{17}/cm^2$ (the oxygen concentration conversion factor certified by the Japan Electronic Industry Development Association - JEIDA). The oxygen concentration of the p^+ substrates was measured by the inert gas fusion infrared spectroscopy (IGF-IR). The oxygen concentration range of the p^+ and p^- substrates was 6.5 to 10.0×10^{17} atoms/cm^3.

The nitrogen concentration of wafers was measured by the secondary ion mass spectroscopy (SIMS). The measured nitrogen concentration range is 0.5 to 3.8×10^{15} atoms/cm^3. The wafers were rapid-heated by lamp to 1,100°C or more for a period of approximately 5 min for heat treatment during the epitaxial layer growth. A wafer with an epitaxial layer deposited on a p^- substrate is called the p/p^- (p on p minus) epitaxial wafer, and another on a p^+ substrate is called the p/p^+ (p on p plus) epitaxial wafer.

For the purpose of investigating the precipitation behavior of the epitaxial wafers, a 2-step heat treatment in a nitrogen atmosphere was applied: the first step at 600 to 900°C for 4 h and the second step at 1,000°C for 16 h. Decrease in oxygen concentration after the heat treatment was measured by the FTIR, and the oxygen precipitate density after the heat treatment by the infrared laser scattering tomography (commercially known as MO-4 of Mitsui Mining make)[6].

The epitaxial wafers were intentionally contaminated with 7×10^{12} atoms/cm^2 of Ni applied on the surface by the spincoat method and lifetime was measured for investigating their gettering abilities. For the lifetime measurement after the contamination, an aluminum metal-oxide semiconductor (Al-MOS) electrode was fabricated on a surface of each epitaxial wafer and epitaxial layer formation lifetime was measured by the MOS-Ct method. Note that the Ni applied on the wafer surface diffuses into the epitaxial substrate during an oxidation heat treatment at 1,000°C for 30 min for oxide film formation during the Al-MOS fabrication process and is absorbed by the gettering sites during a cooling process thereafter.

Additionally, for detail examination of the precipitation behavior of silicon wafers, namely the substrates of the epitaxial wafers, their oxygen concentration decrease and precipitate density were measured after heat-treating them by a single-step heat treatment at 700 to 1,100°C for 8 to 64 h and.

3. Precipitation Characteristics of Nitrogen-doped Epitaxial Wafers

Fig. 3 shows the oxygen precipitation behavior of various p/p^- and p/p^+ epitaxial wafers having different oxygen concentrations. The wafers were heat-treated in two step: 800°C × 4 h + 1,000°C × 16 h. In the figure, the abscissa is the oxygen concentration before the heat treatment and the ordinate is the oxygen precipitate density after it. The nitrogen concentration of the nitrogen-doped epitaxial wafers plotted therein ranges from 0.5 to 1.0×10^{14} atoms/cm^3. Whereas the oxygen precipitate density of the p/p^- and p/p^+ epitaxial

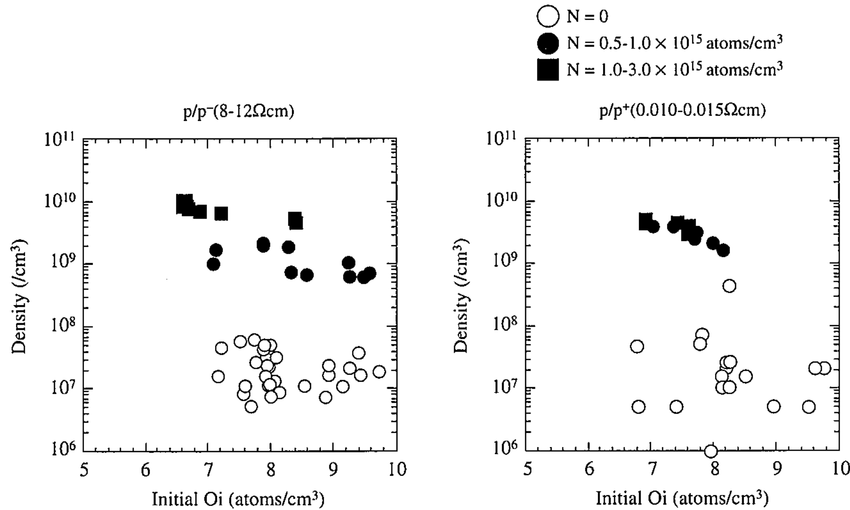

Fig. 3 Precipitate density of epitaxial wafers using nitrogen-doped substrates, after heat treatment for precipitation evaluation ($800°C \times 4$ h + $1,000°C \times 16$ h)

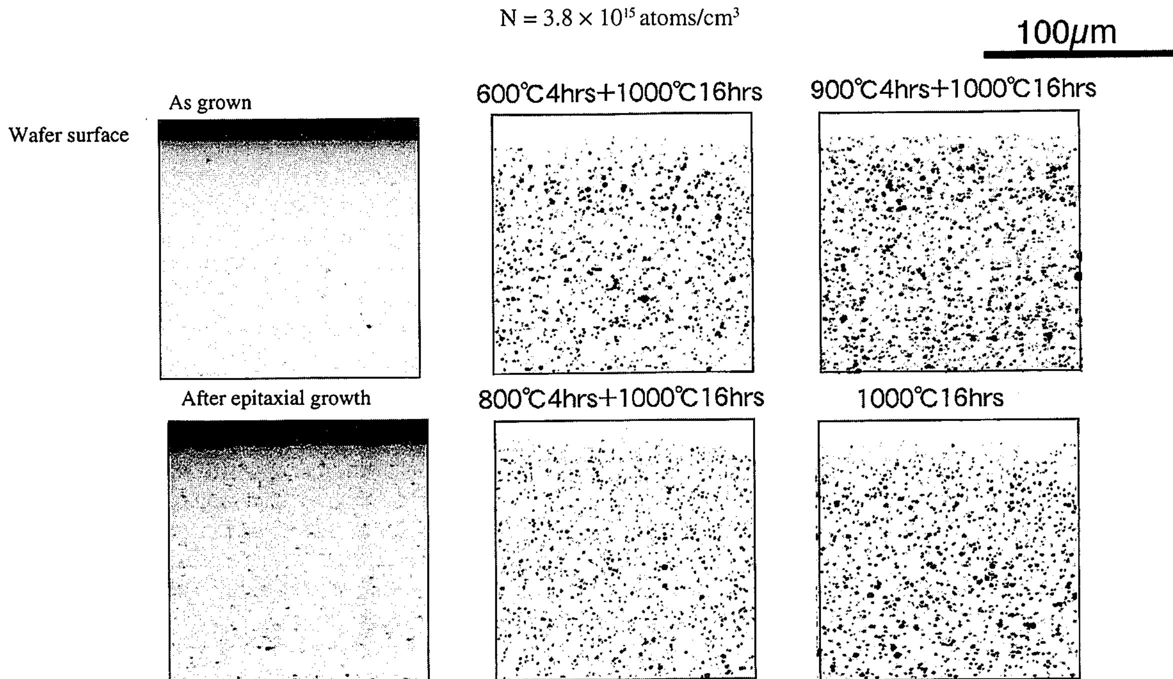

Fig. 4 States of precipitates inside nitrogen-doped epitaxial wafers before and after heat treatment for precipitation evaluation, observed with infrared laser scattering tomography (MO-4)

wafers without the nitrogen addition is 10^8/cm^3 or less, an oxygen precipitate density of 10^9/cm^3 or more is secured in the nitrogen-doped epitaxial wafers. The precipitate density does not depend on the oxygen concentration but is almost univocally determined by the nitrogen concentration. Oxygen precipitation occurs with the silicon wafers without the nitrogen addition when they undergo heat treatment of $800°C \times 4$ h + $1,000°C \times 16$ h.

Grown-in oxygen clusters, which are formed during crystal growth and existent in the wafers before the heat treatment, are considered to work as nuclei of the oxygen precipitate formation during the heat treatment[7]. The reason why oxygen precipitation does not occur after the epitaxial layer deposition is presumably that the oxygen precipitation nuclei disappear during the high temperature processes of the epitaxial layer deposition. In the case of the nitrogen-doped CZ-Si crystals, in contrast, the grown-in oxygen clusters are prospected not to disappear during the epitaxial layer deposition.

Fig. 4 shows results of measurements, using MO-4, of the states of precipitation inside substrates which were cut out from the same crystal but underwent the 2-step heat treatment under different conditions. The figure shows sectional views of the wafers, like in Fig. 2, wherein the black dots correspond to oxygen precipitates. The states of precipitation are shown here as grown and after the epitaxial layer growth. It is understood from the figure that the density of the precipitates is the same regardless of heat treatment condi-

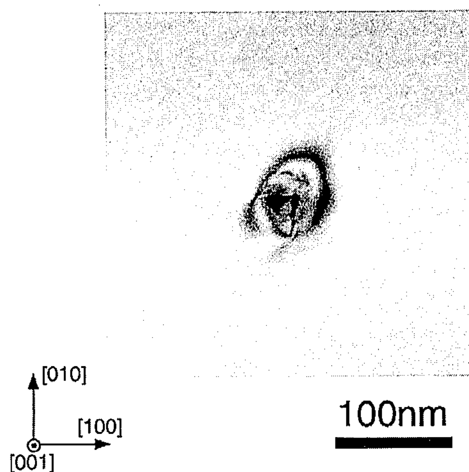

Fig. 5 Grown-in oxygen precipitate in crystal having nitrogen concentration of 3.0×10^{15} atoms/cm^3

tions and that the precipitates have already been formed in the as-grown crystals and also in the wafers after the epitaxial layer growth. We can interpreted this as follows: in the case of the nitrogen-doped crystals, the oxygen precipitates, which survive the epitaxial layer growth process, are formed in the as-grown crystals; and this is the reason for the stable precipitation (that is, stable precipitate density under any heat treatment conditions) unique to the nitrogen-doped epitaxial wafers.

Fig. 5 shows a TEM observation of a grown-in oxygen precipitate in an as-grown nitrogen-doped crystal. The precipitate is roughly 50 nm in size and is characterized by being stretched in a specific crystal direction and surrounded by a strong distortion field. It has been known that the shape of oxygen precipitates in silicon is different depending on the temperature at which they are formed: the oxygen precipitates formed at 1,100°C or higher have an octahedral shape surrounded by {111} facets, whereas those formed at 1,000°C or below are platelets on {100} plane with a distortion field around it[8]. Since grown-in oxygen precipitates in the nitrogen-doped crystal are similar to the latter of the two above, they are suspected to be formed at a low temperature, 1,000°C or below.

It has been confirmed by element analyses that the precipitates comprised oxygen and nitrogen and, from this, the precipitates are considered to form around nuclei of nitrogen and grow while cooling during the crystal growth. Judging from the fact that no precipitates of the size observable by TEM are seen in the CZ-Si wafers without nitrogen addition, it may be considered that the formation of the grown-in oxygen precipitates is a phenomenon unique to the nitrogen-doped crystals.

4. Gettering Behavior of Nitrogen-added Epitaxial Wafers

Fig. 6 shows evaluation of Ni gettering abilities of nitrogen-doped epitaxial wafers. The following p/p$^-$ epitaxial wafers were evaluated for comparison: those without nitrogen addition (oxygen concentration 7.3×10^{17} atoms/cm^3 and 9.5×10^{17} atoms/cm^3), those pre-annealed at 800°C for 4 h before the epitaxial layer growth, and EG epitaxial wafers with a poly-silicon layer deposited on the back side (poly back seal – PBS). Also, the following p/p$^+$ epitaxial wafers were evaluated for comparison: those without nitrogen addition and those pre-annealed at 800°C for 4 h before the epitaxial layer growth.

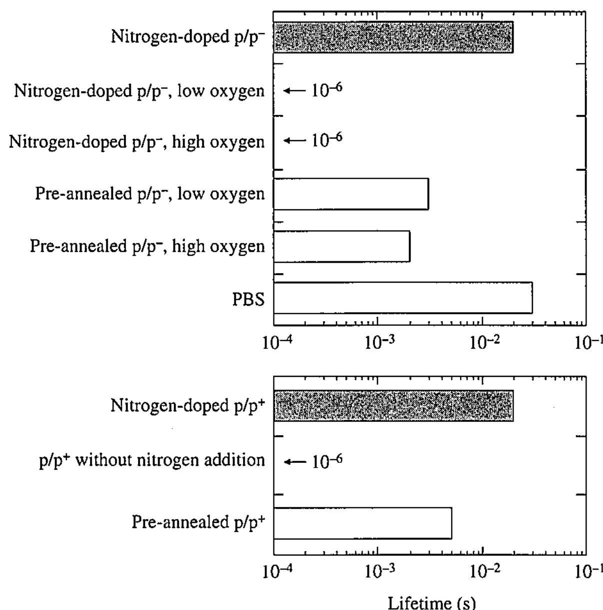

Fig. 6 Lifetime of nitrogen-doped epitaxial wafers after Ni contamination

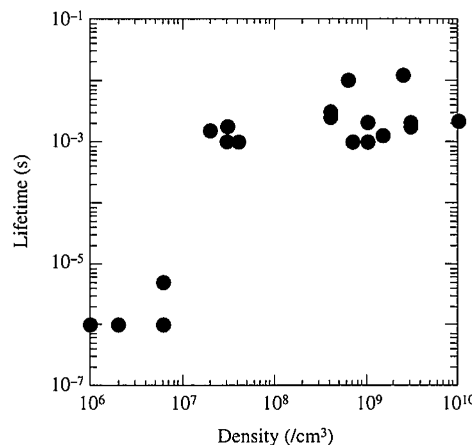

Fig. 7 Relationship between precipitate density in substrate and lifetime

The figure shows that the longer the lifetime value the more Ni is gettered and that, as a result, Ni concentration in the epitaxial layer is decreased. The nitrogen-doped p/p$^-$ epitaxial wafers have the same gettering abilities as the PBS, and the p/p$^+$ epitaxial wafers have higher gettering abilities than the others. **Fig. 7** shows the relationship between the precipitate density and lifetime of the epitaxial wafers with and without nitrogen doping. The lifetime increases rapidly in the range where the precipitate density of the substrates is 10^7/cm^3 or higher and, thereafter, increases as the precipitate density increases, showing increasing stability of the gettering abilities. It is noted in Fig. 7 that the lifetime of the nitrogen-added epitaxial wafers was higher than that of the pre-annealed epitaxial wafers, and that the former showed good gettering properties. When the density of the precipitates is reviewed, which work as the gettering sites, however, while that of the pre-annealed epitaxial wafers is 10^9/cm^3, it is notable that the same of the nitrogen-doped epitaxial wafers is 10^8/cm^3, smaller by one order of magnitude. Although the reason for this is not clear yet, it is suspected that the oxygen precipitates of the nitro-

gen-doped crystals have higher heavy metal absorption capability than those of the crystals without nitrogen addition and, for this reason, they can getter metals contamination effectively despite the smaller density.

5. Precipitation Characteristics of Nitrogen-doped Crystals

Precipitation characteristics of the nitrogen-doped epitaxial wafers manufactured through the epitaxial layer growth on nitrogen-doped wafer substrates were describes above. Oxygen precipitation behavior of the very nitrogen-doped crystals were investigated and the effects of nitrogen on the oxygen precipitation were quantitatively evaluated from a more fundamental viewpoint. The evaluation result is described in this section.

A single-step heat treatment at 700 to 1,100°C in a nitrogen atmosphere was carried out for the evaluation. The maximum treatment time was 64 h to secure sufficient oxygen precipitation. The evaluation methods were the same as those employed in the tests of section 3.

Fig. 8 shows plotting of the oxygen concentration decrease after a single-step heat treatment in relation to the temperature. Whereas the oxygen precipitation of the crystals without nitrogen doping hits a maximum at 900°C, that of the nitrogen-doped crystals increases as the temperature becomes higher. The precipitate density at each heat treatment temperature is shown in **Fig. 9**. Whereas the precipitate density of the crystals without nitrogen doping changes depending on the temperature and hits a maximum at roughly 800°C, that of the nitrogen-doped crystals stays nearly constant except at 700°C. Since the precipitate density of the crystals without nitrogen doping varies depending on the temperature, these crystals have comparatively complex precipitation behavior to hit a maximum precipitation amount at a specific temperature in isochronal heat treatment. In contrast, since the precipitate density of the nitrogen-doped crystals is constant, their oxygen precipitation can be expressed in simple equations.

Fig. 10 shows expression of time-dependency of the oxygen precipitation using the Johnson-Mehl's equation[9], which is as follows:

$$\frac{C_0 - C(t)}{C_0 - C_s} = 1 - \exp(-kt^n) \quad (1)$$

where, $C(t)$: oxygen concentration after a heat treatment time t,
C_s: solid solution concentration of oxygen[10] $(= 9 \times 10^{22} \exp(-1.52/kT))$,
C_0: oxygen concentration before heat treatment.

From the gradients of the plotted $-ln\{(C(t) - C_s)/(C_0 - C_s)\}$ and $log\ t$, the value of n was calculated to be around 3/2 either for the crystals with or without nitrogen addition. This means that the oxygen precipitation behavior shown here is diffusion-limited. While it has been known that the oxygen precipitation of the common crystals without nitrogen addition is oxygen diffusion-limited[11], the above result indicates that the same thing happens also with the nitrogen-doped crystals.

Based on the conclusion that the oxygen precipitation of the nitrogen-doped crystals is diffusion-limited, precipitate growth rates of the crystals were compared with and without nitrogen addition, applying an equation of oxygen diffusion-limited growth expressed by the Ham's equation[12] to the test results. The Ham's equation is as follows:

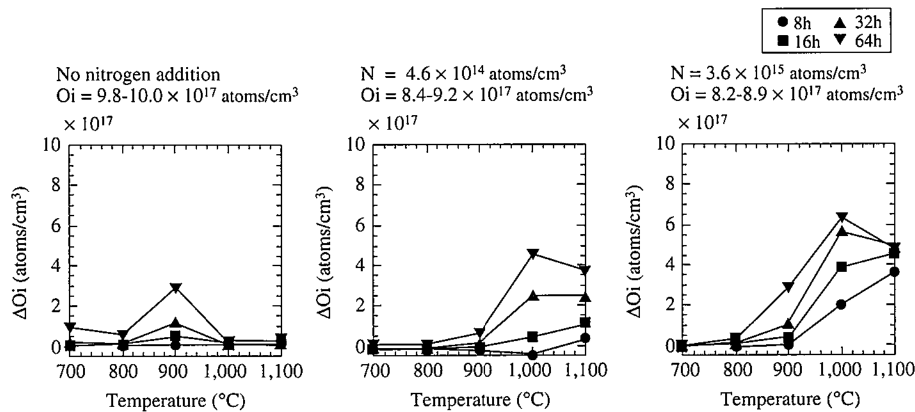

Fig. 8 Oxygen concentration decrease (ΔOi) of crystals having different nitrogen concentrations (after single-step heat treatment)

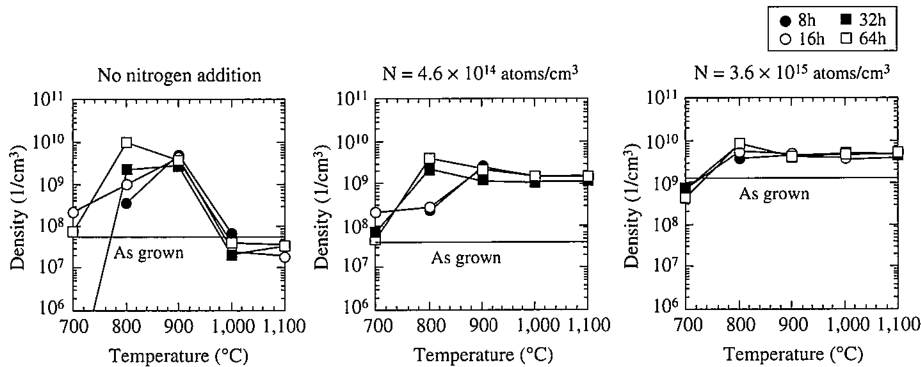

Fig. 9 Precipitate density of crystals having different nitrogen concentrations (as grown and after single-step heat treatment)

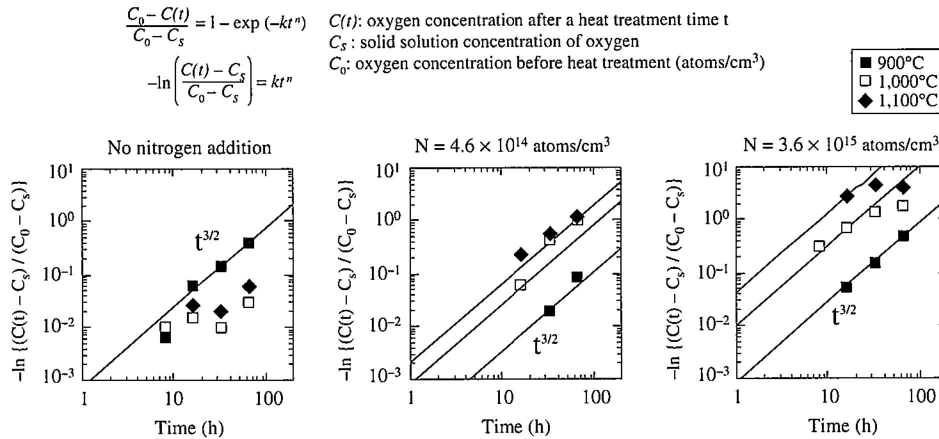

Fig. 10 Time-dependency of oxygen concentration decrease as expressed by Johnson-Mehl's equation

$$\frac{C(t) - C_s}{C_0 - C_s} = \exp\left\{-\left(\frac{t}{\tau}\right)^n\right\} \quad (2)$$

$$\tau = \frac{C_p^{1/3} \cdot r_e^2 \cdot C_0^{2/3}}{2D(C_0 - C_s)} \quad \frac{4\pi}{3} r_e^3 = \frac{1}{N} \quad (3)$$

where, $C(t)$: oxygen concentration after a heat treatment time t,
C_s: solid solution concentration of oxygen ($= 9 \times 10^{22} \exp(-1.52/kT)$),
C_0: oxygen concentration before heat treatment,
C_p: oxygen concentration of precipitates (7.6×10^{22} atoms/cm³ was used assuming SiO_2),
D: diffusion coefficient of oxygen[10] ($= 0.13\exp(-2.53/kT)$),
r_e: radius of equivalent sphere (1/2 of distance between precipitates),
N: precipitate density.

Plotting of the $(C(t) - C_s)/(C_0 - C_s)$ in the case of heat treatment temperature of 900°C in relation to t/τ, we discovered that all its values of the crystals either with or without nitrogen addition were on the same curve, as shown in **Fig. 11**. This indicates that the nitrogen addition does not have any influence whatsoever on the oxygen diffusion rate, which governs the oxygen precipitation rate. Note that, in the tests, the precipitation occurred earlier than was predicted by the precipitation curve calculated from the Ham's equation. This deviation is presumably because the values used as parameters (oxygen diffusion coefficient and oxygen concentration in the precipitates) were unsuitable for the actual conditions, or the measured precipitate density did not reflect the real value. **Fig. 12** shows expression of the oxygen precipitation behavior of the nitrogen-doped crystals at 900 to 1,100°C, in the same manner as Fig. 11. It can be concluded from this that the oxygen precipitation growth of the nitrogen-doped crystals is a diffusion-limited growth with constant precipitate density, at least in the range from 900 to 1,100°C.

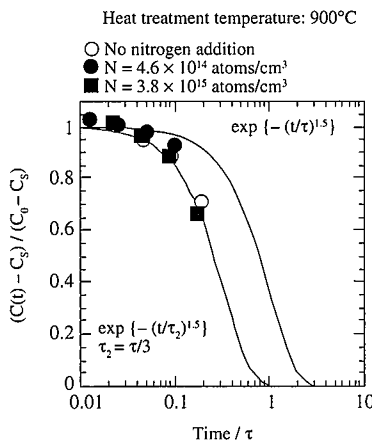

Fig. 11 Time-dependency of oxygen concentration decrease during heat treatment at 900°C (Abscissa is t/τ in Ham's diffusion-limited growth equation.)

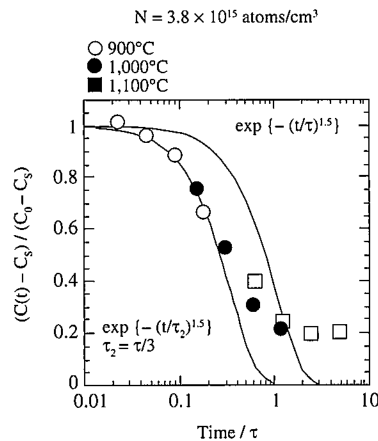

Fig. 12 Time-dependency of oxygen concentration decrease in crystals having nitrogen concentration of 3.6×10^{15} atoms/cm³ during heat treatment at 900 to 1,100°C (Abscissa is t/τ in Ham's diffusion-limited growth equation.)

6. Summary

Nippon Steel Group developed an epitaxial wafer using a nitrogen-doped substrate (nitrogen-doped epitaxial wafer) as a next-generation epitaxial wafer excellent in the IG abilities. This wafer characterizes in being capable of securing high density oxygen precipitates at every kind of heat treatment and has higher gettering abilities of metals contamination compared with common polished wafers without nitrogen addition. The oxygen precipitates of the substrate nitrogen-doped CZ-Si crystal are formed as a result of the growth, during a heat treatment, of the grown-in oxygen precipitates already existent in the as-grown crystals. The growth of the oxygen

precipitates is an oxygen diffusion-limited growth with constant precipitate density and, for this reason, it is simpler and easier to control than the growth of the precipitates in the common CZ-Si without nitrogen addition wherein the precipitate density changes depending on temperature.

The technology of the nitrogen-added epitaxial wafer is expected to play an important role in quality enhancement of the 300-mm diameter epitaxial wafers for the devices conforming to the 0.13 μm design rule.

Reference

1) Ryuta, J., Morita, E., Tanaka, T., Shimanuki, Y.: Jpn. J. Appl. Phys. 29, L1947 (1990)
2) Takeno, H., Ushio, S., Takenaka, T.: Mater. Res. Symp. Proc. 262, 51 (1992)
3) Hourai, M., Nishikawa, H., Tanaka, T., Umeno, S., Asayama, E., Nomachi, T., Kelly, G.: Electrochem. Soc. Proc. 98-1, 453 (1998)
4) Matsushita, Y. et al.: 18th Conf. on Solid State Devices & Mater. Tokyo, p.529
5) Takeno, H., Aihara, K.,Hayami, Y.Kitagawara, Y.: Extended Abstracts, The 44th Annual Spring Meeting, 29a-L-2, The Japan Society of Applied Physics, 1997
6) Moriya, K.: J. Cryst. Growth. 94, 182-196 (1989)
7) Inoue, N., Osaka, J., Wada, K.: J. Electrochem. Soc.: Solid-State Science and Technology. 129 (12), 2780 (1982)
8) Bourret, A.: Mat. Res. Soc. Symp. Proc. 59, 223 (1986)
9) Burke, J.: The Kinetics of Phase Transformation in Metals. Pergamon Press, London, 1965
10) Mikkelesen, J. C. JR: Mat. Res. Soc. Symp. Proc. 59, 19 (1986)
11) Wada, K., Inoue, N.: Cryst. Growth. 49, 749-752 (1980)
12) Ham, F. S.: J. Phys. Chem. Solids. 6, 335-351 (1958)