Extended Abstracts of the 19th Conference on Solid State Devices and Materials, Tokyo, 1987, pp. 235-238

In- and Out-Diffusion and Aggregation of Nitrogen in Si Crystals

Taizo Ito and Takao Abe

R & D Center Shin-Etsu Handoutai Co., Ltd.

2-13-1 Isobe Annaka-shi Gunma-ken, Japan 379-01

Using the out-diffusion profiles of nitrogen doped Si wafers heat-treated at $800-1200^{\circ}$ C measured with the secondary ion mass spectrometry, the diffusivity of nitrogen has been determined as to be D=2.7x10³exp(-2.8eV/kT) cm²/s. This result is five orders of magnitude larger than the other published experimental values. It is observed that nitrogen molecules in atmosphere at elevated temperature can easily in-diffuse into silicon crystals as N-N pairs and aggregate at strained region i.e. dislocations and oxygen precipitates.

1.Introduction

There has been a large number of studies on oxygen, hydrogen, and carbon¹⁾ in silicon crystal which affect electrical properties and generation characteristics of defects in semiconductor device processes. However, there are little interests on nitrogen which is incorporated from nitrogen atmosphere in device processes²⁾. In this study, we clarify three important properties of nitrogen in Si under device fabrication processes;

- 1.large diffusivity compered to oxygen
- in-diffusion from atmosphere at high temperature.
- 3.aggregation of nitrogen to crystal
 defects

2.Diffusivity of Nitrogen in Si crystal

In our experiment, the diffusivity was determined by measuring out-diffusion profiles in nitrogen-doped float-zone(FZ) silicon at crystal growth. The concentration profiles of nitrogen in several heat-treatment samples were measured by secondary ion mass spectroscopy(SIMS). Sample wafers were 500 µm thick with polished sueface. Conditions of the heat-treatments are listed in Table 1. Using CAMECA IMS-3F, we applied 133 Cs⁺ primary ion beam and counted 28 Si¹⁴N⁻ as secondary ion. The SIMS results were calibrated by 14 N ion implanted FZ-Si. The detection limit of nitrogen was found to be 3×10^{14} cm⁻³. Nitrogen concentration of an as-grown sample is determined to be 5×10^{15} cm⁻³.

Typical depth profiles are shown in Fig.1. We observe that the profile(a) fits well with the theoretical curve for diffusivity $2 \times 10^{-8} \text{ cm}^2/\text{s}$ at 1000°C and the profile(b) for $2 \times 10^{-7} \text{ cm}^2/\text{s}$ at 1100°C. To attain the best fit to the experimental data points, the

Table 1.	Heat-treatment	conditions	and
diffusiv	ities.		

Temperature(°C)	Time(min.)	$D (cm^2/s)$
800	1200	1×10^{-10}
1000	15	2×10^{-8}
	30	3×10^{-8}
	60	2×10^{-8}
1100	15	2×10^{-7}
	30	1×10^{-7}
4. 12% of 17	60	1×10^{-7}
1200	5	3×10^{-7}



data with an equation (1).

theoretical curves are obtained by varying parameter D, in an well known solution C(x) of diffusion equation³⁾,

$$C(\mathbf{x}) = \frac{4c_0}{\pi} \sum_{j=0}^{\infty} \frac{1}{2j+1} \sin \frac{(2j+1)\pi x}{h} \exp\left[-\left(\frac{(2j+1)\pi}{h}\right)^2 Dt\right] --(1)^2$$

where C_0 is initial concentration; D, x, and t are the diffusivity, depth, and time, respectively. The solution C(x) is given for the boundary condition in which nitrogen atoms escape from both surfaces of the wafer.

Diffusivities for other samples are listed in Table1. They are also plotted in Fig.2. Activation energy is 2.8eV, and the prefactor is $2.7 \times 10^3 \text{ cm}^2/\text{s}$. From this result, diffusivity at 1100°C becomes $1.4 \times 10^{-7} \text{ cm}^2/\text{s}$. This value is five orders of magnitude larger than the value obtained by Clark et al.⁴⁾. and is four orders larger than the value obtained by Denisova et al.⁵⁾.

To justify the accuracy of our SIMS result and to persuade that nitrogen diffusivity is indeed large, we measured infrared absorption(IR) of nitrogen for a heat-treated sample. Absorption peak at 963 cm^{-1} in IR spectrum is known to be related to nitrogen ⁶⁾.

Two kinds of as-grown samples for the IR measurements are 2mm thick with both sur-



Fig.2 Diffusivity of nitrogen in Si as a function of temperature and measuring methods: SIMS(0) and $IR(\bullet)$. IR result agrees with that of SIMS.

faces polished. Concentrations are determined to be $5.5 \times 10^{15} \text{ cm}^{-3}$ for both samples. After the measurement one of them is submitted to the heat-treatment at 1100°C for 4hours in N₂ atmosphere.

Using a dispersion type double-beam spectrophotometer, relative transmittance of the heat-treated sample is measured versus the as-grown sample with 5.5×10^{15} cm⁻³ of nitrogen.

Resulting difference spectrum is shown in Fig.3. The nitrogen peak in the figure corresponds to the concentration of nitrogen escaped during the heat-treatment. Amount of the escaped nitrogen is evaluated to be $3.3 \times 10^{15} \text{ cm}^{-3}$. From this value the diffusivity at 1100°C becomes $2 \times 10^{-7} \text{ cm/s}$. This agrees with the SIMS result, $1.4 \times 10^{-7} \text{ cm/s}$.

We notice that our value is three orders of magnitude larger than oxygen diffusivity⁷⁾ at 1100°C. Using our data, diffusion length



Fig.3 Difference spectrum of nitrogen in IR measurement. The nitrogen peak hight corresponds to the concentration of escaped nitrogen to be $3.3 \times 10^{15} \text{ cm}^{-3}$, during heat-treated at 1100°C for 4 hours.

 (\sqrt{Dt}) of nitrogen at 1100°C for 10 hours is calculated to be 700µm. This indicates that nitrogen in atmosphere can penetrate through Si wafers by heat-treatment for device fabrication processes.

3. In-diffusion and aggregation in crystal

To observe in-diffusion of atmospheric nitrogen, depth profiles in heat-treated wafers were taken by SIMS. Samples are Czockralski grown, resistivities are 10 Ω -cm and thicknesses are 550 μ m. Oxygen concentration is 9×10^{17} cm⁻³ and nitrogen concentration is below 3×10^{14} cm⁻³. Heat-treatment is performed consecutively as 1100° C+650°C+1000°C in N₂ gas atmosphere.

Solid curve in Fig.4 show the nitrogen and oxygen depth profiles. Because of oxygen out-diffusion, no detect region or denuded zone(DZ) with low oxygen concentration is formed at surface regions of 20µm depth. Supersaturated oxygen in the interior of wafer are precipitated and intrinsic gettering (IG) layer are formed. In DZ region, nitrogen concentration is below the SIMS detection limit as well as the concentration in



Fig.4 Nitrogen and oxygen depth profiles in heat-trated CZ-Si with consecutive temperature ranges at 1100+650+1000°C(solid line) and 1100+650°C(dotted line) in N₂ gas atmosphere.

the as-grown sample. In IG region, nitrogen concentration is detected as high as 5×10^{15} cm⁻³. This concentration is higher than the maximum solubility 4.5×10^{15} cm⁻³ at the melting point in 1420° C⁸⁾. The concentration is maximum at the edge of IG region, and the deeper it from the edge is,the lower the nitrogen concentration is.

Under the heat-treatment with dry 0_2 atmosphere at the same temperature, nitrogen was not detected in IG region but oxygen was precipitated. Comparing the treatment in N_2 atmosphere with the treatment in dry 0_2 atmosphere, it is indicated that atmospheric nitrogen indiffuses very fast and aggregates to the oxygen precipitates and dislocations during the device process heat-treatment.

The dotted lines in Fig.4 show the nitrogen and oxygen profiles after consecutive treatment of 1100+650 °C in N₂ atmosphere. In this condition, oxygen did not precipitated and nitrogen did not aggregate. The last treatment at 1000 °C apparently generates oxygen precipitation and dislocation. We thus conclude that these crystal defects induces nitrogen aggregation to their strain field.

4.Discussion

It is suggested from previously reported IR measurement that incorporated nitrogen in crystalline Si is paired.⁹⁾¹⁰⁾. Absorption peaks of the nitrogen pair vibration appear at 963cm^{-1} and 766cm^{-1} . This decrease of absorption intensity at 963cm^{-1} corresponds to the concentration of reduction of nitrogen pairs.

Consequently the diffusivity obtained in this study should be a value for nitrogen pairs. Then diffusivity of nitrogen pair is three orders of magnitude larger than the value for oxygen. Such a high value is between diffusivity of oxygen and that of metal ion.

Based on the large diffusivity, we make the following comments on the bonding of nitrogen and diffusion mechanism. One nitrogen pair is brige-bonded to Si atoms as same an interstitial oxygen atom. Nitrogen exists as ditomic but oxygen as one atom in interstitial site. Nitrogen pair diffuses by interstitial mechanism like heavy metal impurities. In contrast with this value, previously reported low diffusivities are the value of a substitutional nitrogen atom which is same as other group V elements.

Comment on nitrogen aggregation is as follows. The aggregated nitrogen in Fig.4 is not detected by IR. As the nitrogen concentration measured by SIMS is total amounts with independent of bonding state in the crystal, it is indicates that the aggregated nitrogen are bonded to Si with other bonding state in the diffusion. Because of increasing with the change in bonding state, dissolved concentration decreases so that the indiffusion occurs continuously.

According to the above properties, it is understood why nitrogen locking effect for dislocations is equivalent to oxygen of one hundred times high concentration⁶⁾.

5. Summary

The nitrogen diffusivity is three orders of magnitude larger than that of oxygen. Atmospheric nitrogen molecules can easily penetrate into Si Wafer as N-N pairs. Nitrogen in crystals aggregate to the oxygen precipitation, dislocation, and other high stress region which are generated during heat-treatment in device fabrication processes.

Acknowledment

The authors appreciate to Dr.Y.Kitagawara, Mr.T.Masui and Mr.M.Kimura for helpful advice. The authors also thank Mr.K.Araki for technical assistance.

References

1) "Oxygen, Carbon, Hydrogen and Nitrogen in Crystalline Sillicon" edited by J.C.Mikkelsen, Jr., (Mat.Res.Soc., Pittsuburgh, 1986) 2)P.V.Pavlov, E.I.Zorin, D.I.Tetelbaum, and A. F.Khokhlov, Phys.Stat.Sol.(a) 35, 11(1976) 3)P.G.Shewon:Diffusion in Solid(McGraw-Hill, New York, 1963) 4)A.H.Clark,J.D.MacDougall,K.E.Machester,P.E. Roughan, and F.W.Anderson, Bull.Amer.Phys. Soc.13,376(1968) 5)N.V.Denisova, E.I.Zorin, P.V.Pavlov, D.I.Tetelbaum, and A.F.Khokholov, Izv.Akad.Nauk SSSR, Ser.neorg.Mater., 11, 2236(1975) 6)T.Abe,H.Kikuchi,S.Shirai and S.Muraoka; Semiconductor Silicon 1981, edited by H.R. Huff(Electrochem. Soc., Pennington, 1981)p.54 7) J.C.Mikkelsen, Jr, Appl. Phys. Lett., 40, 336 (19 82) 8)Y.Yatsurugi,N.Akiyama,Y.Endo,and T.Nozaki, J.Electrochem.Soc.120,975(1973) 9)H.J.Stein,Oxygen,Carbon,Hydrogen and Nitrgen in CrystallineSilicon, edited by J.C. Mikkelsen, Jr., (Mat. Res. Soc., Pittsburgh, 1986) p.523 10)T.Abe,H.Harada,N.Ozawa,and K.Adomi, ibid.

p.537