physica **pss** status solidi c
www.pss-c.com
current topics in solid state physics

Germanium-doped Czochralski silicon: a novel material for solar cells

Mukannan Arivanandhan[*,1], **Gotoh Raira**[2], **Kozo Fujiwara**[2], **Satoshi Uda**[2], **Yasuhiro Hayakawa**[1], **and Makoto Konagai**[3]

[1] Research Institute of Electronics, Shizuoka University, Johoku, Naka-ku, Hamamatsu 432 8011, Japan
[2] Institute for Materials Research, Tohoku University, Aoba-ku, Sendai 980 8577, Japan
[3] Department of Physical Electronics, Tokyo Institute of Technology, Okayama, Meguro-ku, Tokyo 152 8552, Japan

* Corresponding author: e-mail arivucz@gmail.com, Phone: +81 53 478 1338, Fax: +81 53 478 1338

The effect of Ge codoping on the light induced degradation (LID) of B doped Czochralski-silicon (CZ-Si) was investigated. The rate of degradation under illumination is relatively suppressed in B and Ge codoped Czochralski-silicon (CZ-Si) compared to B-doped CZ-Si. The O_i concentrations measured by FTIR spectroscopy was decreased as the Ge concentration increased in the Si crystal. The formation of Ge-VO complex in silicon lattice is considered as a possible reason for the variation in O_i. Moreover, the compressive strain field around the Ge-VO complex may increase the barrier for O diffusion which limits the formation of fast diffusing O dimmers. As a consequence, the B-O dimmer (O_{2i}) related defects were relatively suppressed, which causes the suppression of LID effect in B and Ge codoped CZ-Si.
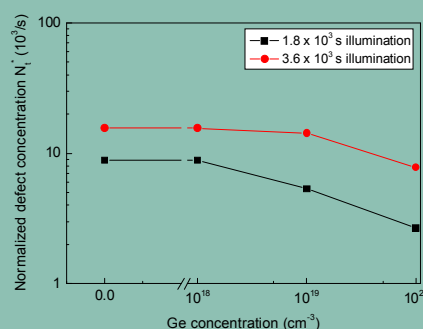
Variations of normalized defect concentration as a function of Ge concentration for two different illumination times (1.8×10^3 and 3.6×10^3 s).

1 Introduction Boron (B)-doped Si is mainly used as a p-type substrate material for solar cells. However, the B-doped oxygen (O) contained Si degrades strongly under illumination which leads to decrease the energy conversion efficiency relatively up to 10% [1]. Thus, the light induced degradation (LID) of B-doped Czochralski-Silicon (CZ-Si), which contains large amount of O, is a serious concern in the photovoltaic industries. The degradation is mainly occurred if B and O are simultaneously present in Si although there is no experimental evidence for the structure of the defect which is responsible for the LID. Based on the experimental results, it is believed that the defect is mainly composed of B and O dimmer (O_{2i}) as the defect concentration is linearly proportional to B concentration and quadratic increase with interstitial O (O_i) [1, 2]. Thus the LID effect can be avoided by eliminating either B or O from Si [3].

The B-O_{2i} defect complexes are acting as a recombination center and trap the minority carriers which results low minority carrier lifetime. Although several approaches and alternatives were suggested for avoiding LID [4, 5], still the LID effect is observed especially in B-doped CZ-Si despite of its vast usage in photovoltaic industries. Recently, high and stable minority carrier lifetime was observed in Ga doped CZ-Si by Ge codoping [6, 7]. In Si lattice, Ge acts as a vacancy trap center [8] which results low flow pattern defect (FPD) and thereby high minority carrier lifetime was observed [7]. However, low segregation of Ga in Si restricts its usage. On the other hand, the formation of B-O metastable defect is relatively suppressed in the presence of Ge and thus the B and Ge codoped CZ-Si shows low degradation effect [9]. Similar kind of beneficial effect was observed by doping Ge into Si [10-12]. However, the influence of Ge on the B-O defect formation is not yet un-

Wiley Online Library

derstood well in detail. As a consequence, further investigations are needed on the effect of Ge in suppression of B-O defect in B doped Si. In the present study, we investigated the LID process in Ge free and Ge codoped Si wafers and the B-O defect generation rate was analysed. Moreover, we measured the O_i concentration in Ge free and Ge codoped CZ-Si by means of Fourier Transform Infrared (FTIR) analysis and the LID suppressing mechanism is discussed based on O_i trapping by Ge-vacancy (V) complex.

2 Experiment

B and Ge codoped <100> Si crystals with various Ge concentrations (10^{18} to 10^{20} cm^{-3}) and fixed B concentration (1×10^{16} cm^{-3}) were grown by CZ method using 11 N purity poly Si. The grown ingots were sliced as wafers and chemically mirror finished using an acid mixture of HF and HNO$_3$ (1:6). The effective minority carrier lifetime on chemically passivated wafers was measured before and after LID by quasi steady state photo conductance (QSSPC) method. B concentration in the crystal was obtained by converting the resistivity data which was measured by four probe resistivity method into carrier concentration using standard ASTM conversion curve [13]. The concentrations of dissolved O_i in the B and Ge codoped CZ-Si wafers were measured by FTIR at room temperature. The O_i in Si exhibits an absorption peak at 1107 cm^{-1} at room temperature. The concentration of dissolved O_i was determined from the absorption coefficient of the peak at 1107 cm^{-1} using the standard calibration factor 3.14×10^{17} cm^{-2} [14].

3 Results and discussion

From the measured data of effective lifetime before (τ_o) and after degradation (τ_d), one can calculate the normalized defect concentrations (N_t^*) using Eq. (1) [1].

$$N_t^* = 1/\tau_d - 1/\tau_o \tag{1}$$

Figure 1 shows the variation of N_t^* as a function of Ge concentration for two different illumination times. As
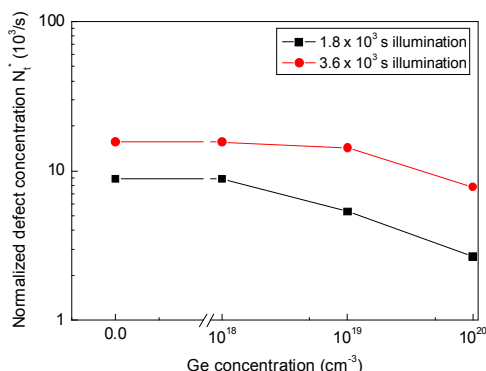

Figure 1 Normalized defect concentration variation with Ge concentration for two different illumination times.

shown in Fig. 1, there was no clear variation in the N_t^* value for the Ge free and Ge (1×10^{18} cm^{-3}) codoped Si wafers. When the Ge concentration was larger than 1×10^{18}

cm^{-3}, the N_t^* value decreased evidently. Moreover, the N_t^* value increases with illumination time in both the Ge codoped and Ge-free wafers. From the measured lifetime data, the defect generation rate ($R_G \equiv 1/\tau_G$) can be determined from the following relation [15]:

$$N(t) = N(t \rightarrow \infty)[1 - \exp(-t R_G)] . \tag{2}$$
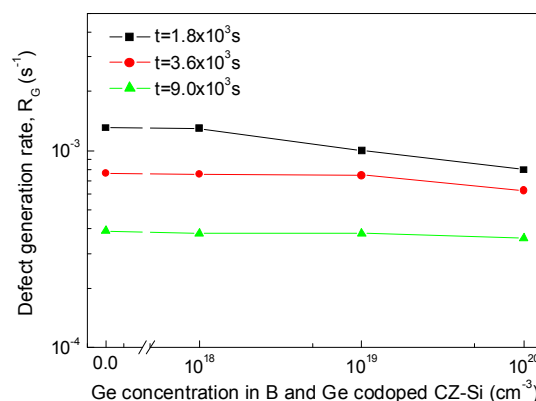
Figure 2 Defect generation rate as a function of Ge concentration for three illumination times (1.8×10^3, 3.6×10^3 and 9.0×10^3 s).
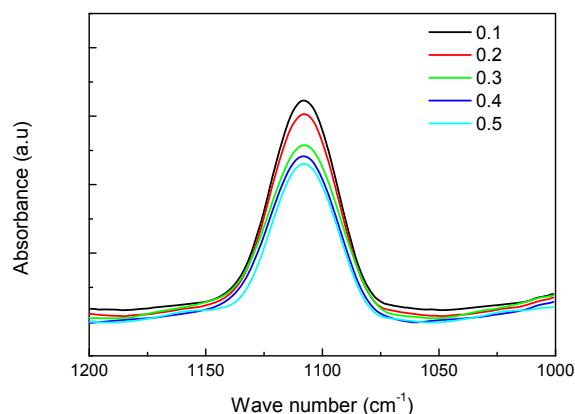
Figure 3 FTIR spectra of heavily (1×10^{20} cm^{-3}) Ge codoped CZ-Si for various solidified fractions.

Figure 2 shows the variation of R_G as a function of Ge concentration for three different illumination times. The defect generation rate was almost the same for Ge free and Ge (1×10^{18} cm^{-3}) codoped Si wafers, whereas the value of R_G decreased evidently when the Ge concentration increased beyond 1×10^{18} cm^{-3}, especially at the initial stage of illumination (1800 s). When the illumination increased the rate of defect generation decreased in both Ge free and Ge codoped Si. After 3600 s of illumination the value of R_G was almost same for Ge free and Ge codoped wafers up to Ge concentration of $\leq 1 \times 10^{19}$ cm^{-3}. Moreover, the value of R_G decreased for the illumination time up to 9000 s for the Ge codoped crystal with Ge concentration of 1×10^{20} cm^{-3} when compared to Ge free and lightly Ge codoped wafers.

The B concentration was found to be same in all the studied samples as it was confirmed from the carrier concentration data of the samples. Figure 3 shows the recorded FTIR spectra for the heavily Ge codoped CZ-Si with various solidified fractions. The intensity of the peak at 1107 cm^{-1} corresponding to O$_i$ decreased when solidified fraction increased. From the peak intensity, the O$_i$ concentration was calculated using the standard conversion factor. Figure 4 shows the O$_i$ concentration variation along the growth direction of the Ge free and heavily (1×10^{20} cm^{-3}) Ge codoped CZ-Si ingots. As shown in Fig. 4, the O$_i$ concentration was relatively low for the heavily Ge codoped Si when compared to Ge free Si. Moreover, the O$_i$ concentration decreased along the growth direction in both crystals, which shows the large segregation ($k_o > 1$) of O in addition with rapid evaporation from melt during CZ-Si crystal growth. Based on the recent defect reaction model proposed by Schmidt et al. [1], fast-diffusing oxygen dimmers O$_{2i}$ are captured by substitutional boron (B$_s$) to form a B$_s$-O$_{2i}$ complex, which are acting as a recombination center and trap the minority carriers. In the present case, as the B concentration was almost the same in all the crystals, the B-O related defect generation during illumination mainly depends on the O$_i$ concentration.
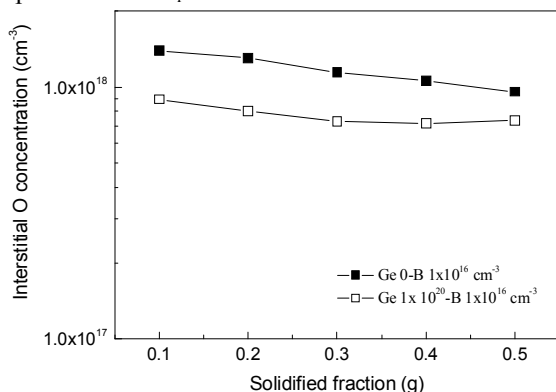
Figure 4 Interstitial O concentration variation in Ge free and heavily (1×10^{20} cm^{-3}) Ge codoped CZ-Si along the growth direction.

It is well known that the O in Si exists in the interstitial state. The binding energy of silicon vacancy (V) with O atom is quite large and thus VO complex (also known as A centers) are possible to form even at high temperature [16]. By forming the A centers, the O moves into substitutional state [17]. As the V has four dangling bonds, it can make bond with either one or two O atoms, which results the formation of VO and VO$_2$ species [17]. In Ge codoped Si, substitutionally placed Ge produces compressive strain in Si lattice as it has larger covalent radius than Si ($\Delta r_{Ge\text{-}Si} = 0.05$ Å). The strain energy produced around the first nearest neighbors of substitutionally doped Ge can be expressed as follows [18]:

$$E^{st} = 4 \times \frac{1}{2} gK_c \left(\Delta r - \Delta r_1 \right)^2 + 8\pi Gr_0 \left(\Delta r_1 \right)^2 , \qquad (3)$$

where gK_c is the stiffness constant, r_o is the inter-atomic distance in Si lattice; G is the shear modulus of elasticity of Si and Δr_1 is the radial displacement of first four nearest neighbors (NN) of Ge, which is smaller than Δr. When V is considered as one of the NN of Ge in Ge doped Si, only three Ge-Si compressive bonds will be formed with one dangling bond (Ge-V). As a result, only three of the NN which make bond with Si moves outward and there is no radial displacement in the vacancy side due to the absence of compressive strain. So, Eq. (3) can be modified as follows after assigning the values of physical constants;

$$E^{st} = (1-\alpha)(9.2 \times 10^{18} \Delta r^2) + \alpha \, (6.85 \times 10^{18} \Delta r^2), \qquad (4)$$

where α is the probability of Ge-V pair formation. When α is zero, the calculated strain energy is 2.26 kJ/mol while the strain energy is reduced to 1.71 kJ/mol when α is one. Thus, Ge-V pair formation in Si is quite favorable in Ge doped Si to relax local strain. Furthermore, the Ge-V pair becomes immobile in Si lattice and trap O$_i$ to form Ge-VO due to large binding energy of VO thereby the Ge-O complex may possible to form. Moreover, the fraction of Ge-O complexes may increase with Ge concentration and it results in the variation of O$_i$ concentration as observed by FTIR analysis (Fig. 3 and 4). Moreover, the IR absorption peak for Ge-O complex could be observed around 1105 cm^{-1}. However, we did not observe any absorption peak at the particular region. It may be difficult to observe in room temperature recorded FTIR spectra possibly due to small fraction of such complex and it may be observed in low temperature IR spectra.

How the O$_i$ is trapped by Ge-V pair and how the Ge influences the trapping process? We hypothesize the mechanism as follows; despite of a large binding energy of vacancy with O$_i$, the vacancy alone cannot effectively trap O$_i$ in the B alone doped Si. This is mainly because the free vacancies diffuse faster in Si lattice with very small migration energy of 0.35 eV [19], thereby the possibility for an O$_i$ to meet and trapped with a vacancy is very small. Moreover, in the B alone doped CZ-Si, the equilibrium vacancy concentration is below the range of 10^{16} cm^{-3} even at high temperature (near melting point of Si) [16], due to large vacancy formation energy of 2.84 eV [20]. On the other hand, the vacancy formation energy is substantially decreased to 1.42 eV in the Ge doped CZ-Si, as shown by the first principle calculations [20]. Moreover, it was experimentally shown that the presence of Ge increases the equilibrium vacancy concentration in Si [21]. As a consequence, it is obvious that the presence of Ge will activate the generation of vacancies at the CZ-Si growth temperature. Further, the vacancies are easily trapped by Ge due to local strain relaxation. Subsequently, the trapped vacancies near Ge become immobile with relatively high migration energy which may further increase the O$_i$ trapping probability. As a result, the large number of O$_i$ is trapped by the Ge-V pair, which leads to a significant retardation of O$_i$ diffusion during illuminations. Moreover, the fast diffusing

Phys. Status Solidi C **10**, No. 12 (2013)

1749

O_{2i} concentration mainly depends on O_i concentration and its diffusion process as the O_{2i} formed by two O_i.

In Ge codoped CZ-Si, the generation of O_{2i} was suppressed by trapping the O_i by Ge through Ge-V complex. Moreover, the compressive strain field around the Ge may increase the barrier for diffusion process of rest of free O_i and thus the O_{2i} concentration was decreased in Ge codoped CZ-Si. It is not worthy to mention that the difference between the normalized defect concentration between Ge free and Ge codoped CZ-Si is larger than the observed O_i concentration variation. Therefore, both the O_i trapping by Ge-V complex and the possible diffusion barrier of compressive strain field around Ge-V complex are responsible for the observed suppression of normalized defect concentration in Ge codoped CZ-Si. The rate of decrease of O_{2i} concentration is possible to increase with increasing Ge concentration as the number of Ge-V pair increased with Ge concentration and thus the number of B-O_{2i} related defects were likely to be decreased with Ge concentration in Ge codoped CZ-Si. Therefore the normalized defect concentration (Fig. 1) and the value of R_G (Fig. 2) were decreased with Ge concentration. As a consequence, Ge codoping into B doped CZ-Si with the concentration of 1×10^{20} cm^{-3} is beneficial for high minority carrier lifetime with relatively low LID.

4 Conclusion

The influence of Ge codoping on the B-O_{2i} defect formation in B-doped CZ-Si was investigated. The normalized defect concentrations related to B-O_{2i} defects were relatively suppressed in Ge codoped CZ-Si compared to Ge free Si. Trapping of O_i by the Ge-V complex and the possible barrier for O_i diffusion by the compressive strain around the Ge-V complex are the possible causes for the suppression of O_{2i} formation. Therefore the B-O_{2i} defects were suppressed in Ge codoped CZ-Si compared to Ge free Si.

References

[1] J. Schmidt and K. Bothe, Phys. Rev. B **69**, 024107 (2004).
[2] J. Schmidt, A. G. Aberle, and R. Hezel, Proc. 26th IEEE Photovoltaic Specialists Conference, Anaheim, California (IEEE, New York, 1999), p. 13.
[3] S. W. Glunz, S. Rein, W. Warta, J. Knobloch, and W. Wettling, Proc. 2nd World Conference on Photovoltaic Energy Conversion, Vienna, Austria (European Commission, Ispra, Italy, 1998), p. 1343.
[4] J. Schmidt and A. Cuevas, Proc. 16th European Photovoltaic Solar Energy Conference 2000, p. 1193.
[5] J. Schmidt, Solid State Phenom. **95-96**, 187 (2004).
[6] M. Arivanandhan, R. Gotoh, K. Fujiwara, and S. Uda, Appl. Phys. Lett. **94,** 072102 (20009).
[7] M. Arivanandhan, R. Gotoh, K. Fujiwara, and S. Uda, J. Appl. Phys. **106,** 013721(20009).
[8] G. D. Watkins, IEEE Trans. Nucl. Sci. **16** 13 (1969).
[9] M. Arivanandhan, R. Gotoh, T. Watahiki, K. Fujiwara, Y. Hayakawa, S. Uda, and M. Konagai, J. Appl. Phys. **111,** 043707 (2012).
[10] T. Fukuda and A. Ohsawa, Appl. Phys. Lett. **60**, 1184(1992).
[11] X. Yu, P. Wang, P. Chen, X. Li, and D. Yang, Appl. Phys. Lett. **97**, 051903 (2010).
[12] P. Wang, X. Yu, P. Chen, X.Li, D. Yang, X. Chen, and Z. Huang, Sol. Energy Mater. Sol. Cells **95** 2466 (2011).
[13] Annual Book of ASTM Standard (1991), Vol. 10.05, Electronics (II), F 723-88 (Am. Soc. Test. Mater. Philadephia, Pennsylvania), p. 508.
[14] H. J. Moller, L. Long, M. Werner, and D. Yang, Phys. Status Solidi A **171**, 175 (1999).
[15] K. Bothe and J. Schmidt, J. Appl. Phys. **99**, 013701(2006).
[16] V.V. Voronkov and R. Falster, J. Cryst. Growth **204**, 462 (1999).
[17] V.V. Voronkov and R. Falster, J. Electrochem. Soc. **149,** G167 (2002).
[18] K. Weiser, J. Phys. Chem. Solids **7**, 118 (1958).
[19] G.D. Watkins, Chin. J. Phys. **15,** 92 (1977).
[20] M. Ganchenkova, A. Nazarov, and A. Kuznetsov, Nucl. Instrum. Methods Phys. Res. B **202**, 107 (2003).
[21] J. Vanhellemont, M. Suezawa, and I. Yonenaga, J. Appl. Phys. **108,** 016105 (2010).