ANNEALING BEHAVIOR OF DONORS FORMED BY HIGH FLEUNCE IRRADIATION OF HIGH ENERGY PARTICLES IN P-TYPE SILICON

H. Matsuura, T. Ishida, Y. Kirihataya, O. Anzawa¹⁾ and S. Matsuda¹⁾ Osaka Electro-Communication University, 18-8 Hatsu-cho, Neyagawa, Osaka 572-8530, Japan

1) National Space Development Agency of Japan, 2-1-1 Sengen, Tsukuba, Ibaraki 305-8505, Japan

Abstract

The hole concentration in B-doped p-type Si is reduced by intermediate-fluence irradiation of high-energy electrons or protons, and this reduction arises from the creation of hole traps as well as the decrease of substitutional B atoms by the irradiation. High-fluence irradiation of high-energy electrons or protons converts p-type conduction into n-type. This type-conversion results from the formation of donor-like defects by the irradiation. Since the donor-like defects are completely annealed out at 523 K, the origin of the donor-like defects is considered to be a complex of an interstitial B and an interstitial O.

1. Introduction

In space, solar cells are exposed to a lot of protons and electrons with high energy. By irradiation, the energy conversion efficiency of solar cells is lowered [1]. The causes of the radiation degradation of $n^+/p/p^+$ silicon (Si) solar cells are classified into three categories [2-7]; (1) the reduction in the diffusion length of electrons in the p layer for low-fluence irradiation, (2) the reduction in the concentration of holes in the p layer for intermediate-fluence irradiation, and (3) the conversion of the p layer to an n layer for high-fluence irradiation. Several types of hole traps are reported to be formed by the low- and intermediate-fluence irradiations, and their origins are discussed [3]. They suggest that the hole concentration should decrease with the fluence. Moreover, from Fourier-transform infrared (FT-IR) measurements at 8 K, the density (N_B) of substitutional boron (B) atoms, which behave as an acceptor, decreases with the fluence [7]. However, the decrease of N_B and the formation of hole traps cannot lead to the conversion of the p layer to the n-layer at all. In order to convert the p layer to the n layer, a lot of donor-like defects must be induced by the high-fluence irradiation. Therefore, the origin of donor-like defects that cause the type-conversion should be clarified.

In this article, we measure the temperature dependence of the hole concentration p(T) in p-type Si irradiated with the intermediate fluence and the temperature dependence of the electron concentration n(T) in n-type Si type-converted by the high-fluence irradiation, and investigate the annealing behavior of donor-like defects or hole traps induced by irradiation. From these experimental results, the origin of donor-like defects induced by the high-fluence irradiation is discussed.

2. Free Carrier Concentration Spectroscopy

Free carrier concentration spectroscopy (FCCS) can accurately determine the densities and energy levels of impurities and traps from Hall-effect measurements [8,9]. Using an experimental p(T) or n(T), the FCCS signal is defined as [8,9]

$$H(T, E_{\rm ref}) \equiv \frac{p(T)^2}{(kT)^{5/2}} \exp\left(\frac{E_{\rm ref}}{kT}\right) \quad \text{or} \quad H(T, E_{\rm ref}) \equiv \frac{n(T)^2}{(kT)^{5/2}} \exp\left(\frac{E_{\rm ref}}{kT}\right) \,. \tag{1}$$

The FCCS signal has a peak at the temperature corresponding to each impurity level or trap level, where E_{ref} is the parameter that can shift the peak temperature of $H(T, E_{ref})$ within the temperature range of the measurement, k is the Boltzmann constant, and T is the measurement temperature. From each peak value and peak temperature, the density and energy level of the corresponding impurity or trap can be accurately determined [10].

3. Experimental

B-doped single-crystalline Si wafers were made by the Czochralski method. The resistivity of the wafers was approximately 10 Ω cm, that is, the B acceptor density (N_A) in the wafers was approximately 2×10^{15} cm⁻³. From radio activation analyses, the oxygen (O) and carbon (C) concentrations in the wafers were determined to be 8×10^{17} cm⁻³ and 1×10^{15} cm⁻³, respectively. The thickness and size of samples for Hall-effect measurements were 220 µm and 5 mm×5 mm, respectively. In order to form good ohmic contacts at four corners of the sample, Ti, Pd and Ag were evaporated on the corners in sequence. Then, the samples were irradiated with 1 MeV electrons or 10 MeV

protons. The fluence of electrons was 1×10^{17} cm⁻², which corresponds to the high fluence. The fluences of protons were between 3×10^{12} cm⁻² and 1×10^{14} cm⁻², which correspond to the intermediate fluence, and also 5×10^{14} cm⁻³, which corresponds to the high fluence.

The Hall-effect measurements were carried out by the van der Pauw method at a magnetic field of 1.4 T. Every measurement was done from 80 K to 420 K. The sample irradiated by electrons was annealed at 523 K in Ar atmosphere for 20 min.

4. Results and Discussion

4.1 Electron irradiation

Figure 1 shows n(T) in the wafer irradiated with the 1×10^{17} cm⁻² fluence of 1 MeV electrons, indicated by solid squares. Here, this measurement was carried out from low temperature to high temperature, called a first measurement. From this result, the p-type wafer is found to be converted to n-type by the irradiation. As is clear from the figure, n(T) decreases with an increase of temperature at >390 K,



Fig.1 Temperature dependence of electron concentration in first measurement (solid squares) and in second measurement (crosses) and hole concentration after annealing (open circles). The sample was irradiated with 1×10^{17} cm⁻² fluence of 1 MeV electrons. All the measurements were carried out from low temperature to high temperature.

while n(T) increases monotonously with T at <390 K. Since it is abnormal that n(T) decreases with increasing T, high temperature during the measurement is expected to reduce the density of donor-like defects formed by the high-fluence irradiation. Therefore, after the first measurement, the measurement was done again from low temperature to high temperature, called a second measurement. This result is also shown by crosses in Fig. 1. Here, in the second measurement, the highest measurement temperature was limited to 300 K in order to avoid annealing donor-like defects due to measurement again. Since n(T) in the second measurement decreases and this is parallel to n(T) in the first measurement, it is clear that donor-like defects induced by the high-fluence irradiation were reduced by the first measurement.

Using n(T) in the first and second measurements, the densities and energy levels of donor-like defects induced by the high-fluence irradiation were determined by FCCS. By the high-fluence irradiation, one type of donor-like defect is found to be mainly formed, and the density $(N_{\rm D})$ and energy level $(E_{\rm C} - E_{\rm D})$ of donor-like defects are determined to be 4×10^{14} cm⁻³ and 0.3 eV below the conduction band minimum $(E_{\rm C})$, respectively, and the compensating density $(N_{\rm comp})$ is estimated to be 2×10^{14} cm⁻³, which is considered to be close to $N_{\rm A}$. The reduction in $N_{\rm B}$ by irradiation was confirmed by FT-IR measurement [7], where $N_{\rm B}$ is considered to correspond to $N_{\rm A}$. The reduction in $N_{\rm A}$ means that some of B atoms do not behave as an acceptor, because the configuration of B in Si is changed by irradiation. From n(T) in the second measurement, $N_{\rm D}$ is found to decrease to 5×10^{13} cm⁻³. During the first measurement, therefore, some of donor-like defects created by irradiation were annealed, and some of B acceptors reduced by irradiation were recovered.

The origin of this donor-like defect is investigated from the annealing behavior of the majority-carrier concentration. From deep level transient spectroscopy (DLTS) and electron spin resonance (ESR) in n-type Si irradiated with the low fluence, the following defects located at around $E_c - 0.3$ eV were reported [11-14]; a divacancy $(V-V)^{-/-}$ at $E_c - 0.23$ eV and $(V-V)^{-/0}$ at $E_c - 0.41$ eV, a complex $(V-O_i)$ of a vacancy and an interstitial O at $E_c - 0.17$ eV, and a complex (B_i-O_i) of an interstitial B and an interstitial O at $E_c - 0.27$ eV. The B_i-O_i is reported to be completely annealed out at >470 K, while the V-V and V-O_i are reported to be completely annealed out at >570 K and >620 K, respectively. Therefore, only B_i-O_i is expected to be completely annealed out

at 523 K.

After the second measurement, the sample was annealed at 523 K in Ar atmosphere for 20 min. The open circles in Fig. 1 represent p(T) after the annealing. In this case, the majority carriers are holes. Therefore, the donor-like defects created by the irradiation are considered to be annealed out at 523K, indicating that this donor-like defect is assigned to B_i-O_i. Moreover, the reason why $N_{\rm B}$ decreased is that high energy electrons kicked some of B atoms from the substitutional site into the interstitial site.

The density (N_{T2}) and energy level ($E_v + E_{T2}$) of the hole trap determined by FCCS using p(T) in Fig. 1 are 2×10^{16} cm⁻³ and 0.3 eV, and N_{comp} is 3×10^{14} cm⁻³, which corresponds to the total density of hole traps at deeper than 0.3 eV and donor-like defects. Here, E_v is the valence band maximum. This suggests that the hole traps were not annealed out while the donor-like defects were annealed out at 523 K. Moreover, it indicates that a large amount of hole traps was created by the high-fluence irradiation.

4.2 Proton irradiation

Figure 2 shows a set of five p(T) in the samples irradiated with five different fluences of 10 MeV protons (open triangles: 3×10^{12} , solid inversed triangles: 1×10^{13} , open squares: 3×10^{13} , solid circles: 6×10^{13} , and crosses: 1×10^{14} cm⁻²) and one n(T) in Si irradiated with 5×10^{14} cm⁻² fluence, indicated by open circles. From these experimental results, it is confirmed that the type-conversion occurs at the 5×10^{14} cm⁻² fluence of 10 MeV protons. In the cases of fluences between 3×10^{12} and 6×10^{13} cm⁻², p(T) in the second measurement coincides with p(T) in the first measurement. For example, Fig. 3 shows a set of two p(T) in the 6×10¹³ cm⁻² fluence in the first measurement (solid squares) and in the second measurement (crosses). This indicates that the reduction in p(T) by irradiation does not result from the donor-like defect (i.e., B_i - O_i) and that hole traps created by these irradiations cannot be annealed out below 400 K. FCCS detects two types of hole traps at ~ 0.2 eV and ~ 0.3 eV above E_v in these samples.

Figure 4 displays a set of two p(T) in the sample irradiated with 1×10^{14} cm⁻² of 10



Fig. 2 Fluence dependence of hole concentration in Si irradiated by 10 MeV protons.



Fig. 3 Temperature dependence of hole concentration in Si irradiated with 6×10^{13} cm⁻² fluence of 10 MeV protons in first measurement (solid squares) and in second measurement (crosses). The measurements were carried out from low temperature to high temperature.

MeV in the first measurement (solid squares) and in the second measurement (crosses). In this case, heating the sample up to 400 K in the first measurement recovers p(T), indicating that the large reduction in p(T) by the 1×10^{14} cm⁻² fluence irradiation mainly arises from the creation of B_i-O_i by the irradiation.

From the discussion mentioned above, the reduction in p(T) arises from the creation of hole traps in the case of the intermediate fluence, while the reduction is mainly caused by the formation of B_i-O_i in the cases of 1×10^{14} cm⁻² close to the high-fluence.

5. Conclusion

B-doped p-type Si was converted into n-type by high-fluence irradiation (>1×10¹⁷) cm⁻² fluence of 1 MeV electrons or $>5 \times 10^{14}$ cm⁻² fluence of 10 MeV protons). From the annealing behavior of the majority-carrier concentration, the type-conversion is found to arise from the donor-like formation of defects by irradiation. Since the donor-like defects can be annealed out at <523 K, they are assigned to a complex of an interstitial B and an interstitial O, which is formed by the high-fluence irradiation.



Fig. 4 Temperature dependence of hole concentration in Si irradiated with 1×10^{14} cm⁻² fluence of 10 MeV protons in first measurement (solid squares) and in second measurement (crosses). The measurements were carried out from low temperature to high temperature.

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