ABSTRACT

Damage produced in n-type silicon by neutron irradiation at room temperature was studied by deep-level transient spectroscopy (DLTS) and compared with 2 MeV electron damage. The similarities and differences between neutron and electron damage were shown. It was found that point defect character predominated even in the neutron case as far as the DLTS measurements are concerned, and that the same defects as those in the electron case, i.e., the A center, E center and divacancy, were produced by room temperature neutron irradiation. However, the production of the divacancy was important in the neutron damage, while the production of the A center was important in the electron damage. This was attributed to the difference of the energy of the primary knock-ons between neutron and electron irradiation. The formation of several defects during annealing in neutron irradiated n-type silicon was reported also.

I. Introduction

There have been many studies of the radiation damage and annealing behavior in fast-neutron-irradiated silicon from the Hall-effect measurements, lifetime measurements, and infrared absorption and photoconductivity measurements. Recently, the energy levels of defects produced by neutron irradiation at room temperature have been determined using junction devices with various kinds of measurement techniques. Among these techniques, the deep-level transient spectroscopy (DLTS) is the most useful one for its highly sensitive sensitivity of defects. The DLTS measurements have indicated that three energy levels ($E_a = -0.15$, $E_a = -0.21$ and $E_a = -0.39$ eV) in n-type silicon and two energy levels ($E_a + 0.15$ and $E_a + 0.34$ eV) in n-type silicon are created in the forbidden gap by neutron irradiation.

It is well known that fast neutrons produce defect clusters in silicon because of the high energy of the primary knock-ons, and the phenomena different from those in gamma-ray and electron-irradiated silicon have been observed. Stein has reported that defect clusters produced at liquid nitrogen temperature recover in diffuse stages with annealings up to 277°C. On the other hand, it has been reported that the formation of the E center (vacancy-phosphorus complex) A center (vacancy-oxygen complex) and divacancy occurs during annealing in silicon below room temperature. The formation of these defects is attributed to the vacancy liberation from defect clusters.

In the present paper, with DLTS measurements, we investigate the damage produced in n-type silicon by neutron irradiation at room temperature and compare it with the 2 MeV electron damage. The similarities and differences between neutron and electron damage are shown and discussed. The formation of several defects during annealing in neutron-irradiated n-type silicon is reported also.

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Fig. 1. DLTS spectra after neutron irradiation and after 330°C annealing for n-type silicon with the resistivity of 0.8 - 1.2 Ohm. Three defects E1 ($E_a = -0.21$ eV), E2 ($E_a = -0.39$ eV), and E3 ($E_a = -0.15$ eV) are shown.

II. Experimental Procedure

The samples used were p-type diodes fabricated by diffusing boron into phosphorus-doped Czochralski-grown silicon wafers with resistivities of 0.2 - 0.4 and 0.8 - 1.2 Ohm. The total neutron fluxes ($Q_n$) are 5x10^{13} and 1x10^{14} neutrons/cm² for samples with resistivities of 0.2 - 0.4 and 0.8 - 1.2 Ohm, respectively. 2 MeV electron irradiation was performed at room temperature using the resonance transformer accelerator at Takasaki Radiation Chemistry Research Establishment of Japan Atomic Energy Institute. For samples with the resistivity of 0.8 - 1.2 Ohm, the total electron flux ($Q_e$) is 5x10^{13} electrons/cm². Isochronal annealing experiments were carried out in the temperature range 60 - 350°C with 2°C temperature control. The isochronal annealing period was 20 min, and the temperature increment was 30°C.

The DLTS measurements were performed for these samples. The capacitance was measured using a Boonton 72BD capacitance meter. The DLTS method with a bipolar rectangular weighting function was used in the present work. The DLTS measurement technique and apparatus have been given in detail previously.

III. Experimental Results

A. Isochronal Annealing Results of Neutron-Produced Defects

The DLTS spectra after irradiation and after 330°C annealing are shown in Fig. 1 for a sample with the resistivity of 0.8 - 1.2 Ohm. Three defects E1 ($E_a = -0.21$ eV), E2 ($E_a = -0.39$ eV), and E3 ($E_a = -0.15$ eV) are shown. The isochronal annealing period was 20 min, and the temperature increment was 30°C.
Fig. 2. Time constant \( \tau \) versus reciprocal temperature for the defects E4 and E5 observed in neutron-irradiated n-type silicon during annealing.

0.15 eV), E2 (\( E_c = 0.21 \) eV) and E3 (\( E_c = 0.39 \) eV) are produced by neutron irradiation, which has been reported previously\(^\text{17}\). On the other hand, two defects E4 and E5 are observed in the DLTS spectrum after 330 °C annealing. In Fig.2, the time constant \( \tau \) for the defects E4 and E5 is shown as a function of reciprocal temperature. The time constant \( \tau \) is related to the electron emission rate \( n_e \) as follows

\[
\tau = \frac{1}{n_e} = \frac{1}{v_n \sigma_n N_c \exp \left( \frac{E_F - E_c}{kT} \right)}
\]

where \( v_n \) is the average electron thermal velocity, \( \sigma_n \) is the electron capture cross section, \( N_c \) is the effective density of states in the conduction band, \( E_c \) is the energy of the conduction band, and \( E_c \) is the energy level for defects. The energy levels of the defects E4 and E5 were estimated to be \( E_c = 0.31 \) and \( E_c = 0.45 \) eV, respectively from the temperature dependence curves of the time constant assuming a \( T^{-2} \) temperature dependence for the pre-exponential factor of the time constant\(^\text{17}\). The electron capture cross sections of the defects E4 and E5 were \( 5.4 \times 10^{-17} \) and \( 1.2 \times 10^{-18} \) cm\(^2\), respectively.

Fig. 3. Isochronal annealing behavior of defects in neutron-irradiated n-type silicon. In the figure, \( N_c \) represents the defect concentration.

In Fig.3, the isochronal annealing behavior of the defects E1 - E5 is shown. The defects E3 has two annealing stages around 120 and 280°C. The defect E2 disappears around 300°C annealing. It seems that the annealing behavior of the defects E2 and E3 in the temperature range 200 - 300°C are similar. The E1 defect shows complicated annealing behavior. In the annealing temperature range 90 - 150°C, growth of the defect E1 occurs. It is interesting that this temperature range corresponds to the first annealing stage of the defect E3. Furthermore, in the temperature range 240 - 300°C, little recovery of the defect E1 is observed in spite of the annealing in the temperature range 150 - 240°C. On the other hand, the defect E4 begins to grow around 240°C and disappears around 360°C. The defect E5 is observed in the annealing temperature range 330 - 360°C. In the following section, these results are compared with those obtained for the 2 MeV electron-irradiated n-type silicon.

B. Comparison of Neutron and 2 MeV Electron Damage

1. Similarities Between Neutron and Electron Damage

The DLTS spectra after neutron and 2 MeV electron irradiation are shown in Fig.4 for samples with the resistivity of 0.8 - 1.2 Ωcm. It is found that the positions of the peaks in the DLTS spectra coincide with each other. In Fig.5, the isochronal annealing behavior of electron-produced defects is shown to compare with that of neutron-produced defects in Fig.3. The growth of several defects during annealing was observed in electron-irradiated n-type silicon as previously reported by other investigators\(^\text{21,22}\), although this was not shown in Fig.5. It is seen from Figs.3 and 5 that the isochronal annealing behavior of neutron-produced defects is similar to that of electron-produced defects. These results indicate that defects produced by neutron irradiation are the same as those by electron irradiation. However, the magnitude of the growth of the defect E1 around 120°C is smaller in the electron case. This is discussed later.

It has been reported that the A center (vacancy-oxygen complex), E center (vacancy-phosphorus complex) and divacancy are produced in n-type silicon by electron irradiation\(^\text{1-23}\). The energy level and annealing-out temperature of the defect E1 are in good
agreement with those of the A center. The energy levels of the defects E2 and E3 are in agreement with those of the double and single-minus charge states of the divacancy, respectively. Furthermore, the annealing-out temperatures of the defects E2 and E3 coincide with that of the divacancy. It is considered that the defects E2 and E3 associate with the double and single-minus charge states of the divacancy, respectively. However, if the defects E2 and E3 associate with the different charge states of the divacancy, the production rates of the defects E2 and E3 should be identical, which contradicts the present results as seen from Figs. 3 and 5. Here, it is noted that the defect E3 has two annealing stages. The first stage of the defect E3 corresponds to the annealing stage of the E center rather than the divacancy. Furthermore, at the end of the first stage, the concentration of the defect E3 is approximately equal to that of the defect E2, and then the defects E2 and E3 show almost the same annealing behavior. These results suggest that the defect E3 consists of two different defects, that is, the E center and single-minus charge state of the divacancy. It is possible that the close energy levels between the E center (Ec = 0.44 eV) and the single-minus charge state of the divacancy (Ec = 0.39 eV) or the close time constants between them make it difficult to resolve them in the DLTS measurements. Gregory et al. have observed the production of the energy levels of Ec = 0.36 and Ec = 0.44 eV in neutron-irradiated n-type silicon from the measurements of the large signal pulse response of the junction field-effect transistors. On the other hand, from Figs. 3 and 5, it is found that the first stage of the defect E3 corresponds to the temperature range where the growth of the defect E1 occurs. Ewarsayé has reported that the A center grows as the vacancy-arsenic complex recovers in 1.5 MeV electron-irradiated arsenic-doped silicon. He has shown that the release of vacancies due to the dissociation of the vacancy-arsenic complex results in the formation of more A centers. It is possible that the same mechanism acts in the growth of the A center in phosphorus-doped silicon. In order to confirm this speculation, the isochronal annealing behavior of the defects E1 and E3 in neutron-irradiated silicon was investigated for samples with different phosphorus concentrations (4.5 x 10^{15} and 1.2 x 10^{16} cm^{-3}). This comparison is shown in Fig. 6, where the defect concentrations are normalized to those after irradiation. In Fig. 5, the isochronal annealing behavior of the defects E1, E2 and E3 in 2 MeV electron-irradiated n-type silicon is shown. In the figure, N0 represents the defect concentration.
fect concentration is shown in Fig. 7 for neutron and electron-irradiated samples with the resistivity of 0.9 - 1.3 Ωcm. The total defect concentration was obtained by adding each defect concentration observed at each annealing temperature. Then, the defect E2 concentration was excluded to avoid adding the divacancy concentration twice. In Fig. 7, the total defect concentration is normalized to that after irradiation. A difference is observed around 270°C. The growth of several defects during annealing was observed around 270°C for both neutron and electron-irradiated n-type silicon. However, in the electron case, the isochronal annealing behavior of the total defect concentration is dominated by that of the A center since the concentration of the A center is extremely larger compared to those of other defects. This result coincides with that reported by Walker and Sah.21 On the other hand, in the neutron case, the growth of the total defect concentration is observed around 270°C. This temperature range corresponds to the annealing temperature range of the divacancy. It is considered that the growth of defects during annealing around 270°C is due to the annealing of the divacancy. The difference observed around 270°C again shows the increasing importance of the divacancy in the neutron case.

IV. Discussion

In Sec. III, the similarities and differences between neutron and electron damage were shown. Summarizing these results, it is found that defects produced by neutron irradiation are the same as those by electron irradiation. The defects E1 and E2 correspond to the A center and the double-minus charge state of the divacancy, respectively, and the defect E3 consists of two different defects, that is, the E center and the single-minus charge state of the divacancy. However, the production of the divacancy is more important in the neutron case.

Kimerling22 has reported that the production of the divacancy is increasingly important with the heavier or more energetic particles (alpha particles, and 1 and 10 MeV electrons). Kimerling's result and ours suggest that the higher energy of the primary knock-ons leads to the increasing importance of the divacancy. The divacancy is produced directly as a multiple-displacement defect in the primary radiation event or indirectly as a combination of two vacancies23,24. On the other hand, the A center and E center are formed by trapping vacancies at impurity sites. Especially, oxygen has a good effect for the vacancy. Therefore, the production and motion of the vacancy are studied by monitoring the production and growth of the A center.7 It is well known that fast neutrons produce defect clusters because of the high energy of the primary knock-ons25. Whan26 has shown that the production rate of the A center is extremely low in neutron-irradiated silicon at ~50°C, which indicates that the production rate of the vacancy is low in the neutron case. Also, the growth of the A center upon annealing to 275°C was shown. This is attributed to the vacancy liberation from defect clusters. It is considered that the A center observed here is formed due to the vacancy liberation from defect clusters during room temperature irradiation. The E center should be formed in a similar manner to the A center. Furthermore, Stein3 has indicated that the major fraction of the divacancy observed in room temperature neutron-irradiated silicon are formed as secondary defects rather than being formed directly upon irradiation. It was reported that the formation of the divacancy is due to the same mechanism as the A center. Therefore, it follows that the same defects as those in the electron case are produced with room temperature neutron irradiation. However, it seems that the probability of the combination of two vacancies is high in the neutron case since the vacancies are produced in a localized region. This will suppress the formation of the A center, which coincides with the present results. On the other hand, in the electron case, vacancies are produced homogeneously in the material. This leads to the relatively larger production rate of the A center.

The production and annealing behavior of the A center and divacancy in neutron-irradiated silicon have been investigated with infrared absorption measurements.7,8 Cheng and Lori9 have reported that the ratio of the production rate of the divacancy to that of the A center at room temperature irradiation is 40 and 13 for different oxygen concentrations (1x1017 and 1.8x1018 cm⁻³). However, in the present experiments, its ratio is only 0.31 although it is much larger than the ratio 0.048 in the electron case. Infrared absorption measurements also have indicated that the growth of the A center occurs in the temperature range ~50 to 275°C due to the vacancy liberation from defect clusters. However, such a growth is not observed in the DLTS measurements. The growth of the A center observed in the temperature range 100 - 150°C is explained by the release of the vacancy from the A center rather than from the defect clusters as shown in Fig. 6. It is noted that little recovery of the defect E1 is observed in the temperature range 240 - 300°C as shown in Figs. 3 and 6. In this temperature range, the growth of defects occurs. It is possible that the growth of the A center occurs also. However, little recovery of the defect E1 in the temperature range 240 - 300°C is observed even in the electron case as shown in Fig. 5. To our knowledge, this annealing behavior has not been previously reported. Further investigations are necessary to explain this annealing behavior. On the other hand, infrared absorption measurements have shown that the annealing of the divacancy extends over a broad temperature range 100 - 350°C, which is not observed in the DLTS measurements. The discrepancies between the DLTS and infrared absorption measurements may be due to the large difference of neutron fluxes. The neutron fluxes used in the infrared absorption measurements are two to three orders of magnitude larger than those in the present DLTS measurements. Neutron fluxes of the order of 10¹⁶ neutrons/cm⁻² in the infrared absorption measurements leads to heavy damage, and overlapping of defect clusters may occur. The results observed with infrared absorption measurements have a good time to explain the production of defect clusters. On the other hand, the present DLTS measurements indicate that point defect character predominates even in the neutron case. However, it has been reported that the production of defect clusters is still observed with Hall effect and minority carrier lifetime measurements at the neutron fluxes of the order of 10¹³ neutrons/cm². These suggest that varying results are due to different measurement techniques. It seems that the growth of defects around 270°C annealing as shown in Fig. 7 is due to the annealing of defect clusters in addition to that of the divacancy since defect clusters recover in diffuse stages with annealing up to 275°C.22

V. Conclusions

Neutron damage in n-type silicon was studied by deep-level transient spectroscopy (DLTS). Isochronal annealing behavior of neutron-produced defects (E1, E2 and E3) was given, and the formation of the defects E4 (EC - 0.31 eV) and E5 (EC - 0.45 eV) during annealing was reported.
These results were compared with those obtained for 2 MeV electron-irradiated n-type silicon. It was found that defects produced by neutron irradiation were the same as those by electron irradiation and that the defects E1 and E2 corresponded to the A center and the double-minus charge state of the divacancy, respectively. Also, the defect E3 consisted of two different defects, namely, the E center and the single-minus charge state of the divacancy. However, the production rate of the A center was extremely large in the electron case, while the production of the divacancy was more important in the neutron case. This was attributed to the difference in the energy of the primary knock-ons between neutron and electron irradiation.

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