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The optically active process of higher-order bands in neutron-irradiated silicon

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Abstract. The optically active process of higher-order bands (HOBs) in fast-neutron-irradiated float-zone silicon has been investigated at low temperature using a Fourier-transform infrared spectrometer with optical excitation. It is found that the photoexcitation process follows an exponential time dependence and that the decay is logarithmic with a decay time constant of 10^5 s at 7 K. The saturation value of the absorption coefficients depends on the logarithm of the illumination-light intensity. These characteristics are associated with the slow relaxation of photoexcited carriers originating mainly from defect clusters. The relaxation behaviour of photoexcited carriers has been analysed using the macroscopic-barrier model, which is in good agreement with the observations.

1. Introduction

There has been a considerable experimental and theoretical effort towards the understanding of defect properties under optical excitation. Examples of these include DX centres in $Al_xGa_{1-x}As$ [1, 2], EL2 in GaAs [1, 3, 4], and radiation-induced defects such as C_sC_i pairs [5, 6] and higher-order bands (HOBs) [7–9] in Si. Here, our study is concentrated on the optically active process of the HOBs in fast-neutron-irradiated Si.

Neutron radiation introduces a huge number of complex defects, which govern the properties of the semiconductor. The characteristics of neutron-radiation-induced defects, especially defect clusters, are different from those induced by other kinds of particle, due to the heavy radiation damage and the penetration of neutrons. The HOB appears only in Si irradiated with a high fluence of fast neutrons followed by annealing at 400–600 °C. It consists of more than 40 sharp bands in the wavenumber range of 600–1400 cm^{-1}, which have been identified as electronic transitions [10–12]. It is believed that the defect related to the HOB comprises a family of at least three intrinsic defect complexes involving vacancies and/or interstitials. In neutron-irradiated Si, in particular float-zone (FZ) Si, the Fermi level is pinned around the middle of the band gap due to the radiation damage. To observe the HOB, therefore, band-edge illumination leading to the shift of the quasi-Fermi level is required. An interesting observation of the photoexcitation and decay of the HOB was reported by Corelli and co-workers [7] based upon an examination of the residual absorption in neutron-irradiated FZ silicon. This led Corelli to suggest the defect related to the HOB has three charge states within the band gap, where the intermediate state is a strong trap and the final state gives rise to the HOB. Recently, this optically active process of the HOB was proposed to be associated with a slow relaxation process of photoexcited carriers

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[8, 9]. Apparently, the characteristics of photoexcitation and decay are very important for the understanding of the HOB.

Slow relaxation of photoexcited carriers including persistent photoconductivity in various semiconductors is complex. It involves many aspects of a semiconductor: optical absorption, carrier recombination kinetics, lifetime-controlling defects and transport properties. Several models have been proposed [13, 14]. The phenomena of slow relaxation of photoexcited carriers in neutron-irradiated silicon have been observed with persistent photoconductivity measurements [15, 16], and analysed with the macroscopic-barrier model associated with fast-neutron-induced defect clusters. However, no detailed investigation on this system at low temperatures has been performed so far, and the relation of the photoexcitation and decay of the HOB with the relaxation process of photoexcited carriers, for instance, has still to be confirmed. In the present paper, we investigate in detail the photoexcitation and decay of the absorption of the HOB in fast-neutron-irradiated FZ Si at low temperature under optical excitation. The relaxation behaviour of photoexcited carriers is analysed using the macroscopic-barrier model.

2. Samples and experimental procedures

The samples studied in this experiment were extracted from a FZ-Si crystal of high resistivity ($> 2000\ \Omega$ cm), and irradiated at room temperature with a high fluence of fast neutrons (8×10^{18} cm^{-2}, neutron energy $E_n > 1.0$ MeV) in a light-water reactor. The samples were sealed within evacuated quartz capsules and annealed at different temperatures in the range of 300–600 °C, particularly at 450 °C, for different annealing times from 10 min to 100 h.

Infrared absorption measurements were performed with a JEOL JIR-100 Fourier-transform infrared (FTIR) spectrometer at low temperatures. The temperature was controlled by an Air Products liquid-helium cryostat in the range from 6 to 300 K. Spectral resolutions were from 0.25 to 2 cm^{-1} in accordance with the requirements of measurements. The light source of the spectrometer was filtered with a Ge wafer at room temperature for all measurements. The samples were cooled in darkness, and were measured with or without additional illuminating light, obtained from a W lamp through a monochromator. Conventional Hall-effect measurementes were used to determine the position of the Fermi level.

3. Experimental results

Absorption bands related to the HOB are observed in those samples annealed in the temperature range of 400–600 °C, the strongest absorption being obtained in the samples annealed at 450–500 °C. The present investigation is focused on the samples annealed at 450 °C. Although the absorption coefficient of each absorption band varies in differently annealed samples, the positions of the prominent absorption bands do not change. These absorption bands broaden slightly with an increase of sample temperature, and disappear above 90 K. Figure 1 shows typical infrared absorption spectra of the HOB in the sample annealed at 450 °C for 40 h and measured at 7 K. The absorption bands cannot be detected before illumination (figure 1, spectrum A). The band O_i at 1136 cm^{-1} is the absorption arising from the localized vibration of interstitial O atoms [17]. More than 40 sharp absorption bands are clearly visible under illumination (figure 1, spectrum B), the positions

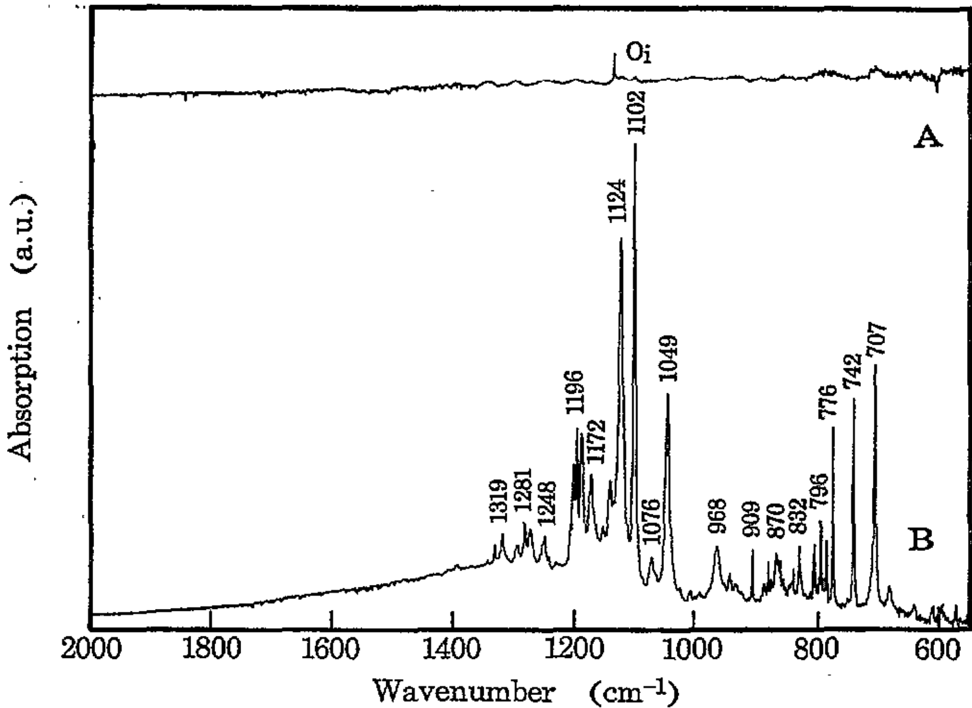

Figure 1. Infrared absorption spectra at 7 K of the sample annealed at 450 °C for 40 h: spectrum A, measured without illumination, and spectrum B, measured with band-edge light illumination.

of the prominent absorption bands being labelled. These observations are made after annealing up to 100 h.

Due to heavy radiation damage, the Fermi level is pinned near the middle of the band gap in the present samples even after annealing at 450 °C for 100 h, as shown in figure 2. These data are deduced from the Hall-effect measurements at 300 K. At low temperatures, the resistivity in these samples is too high to be measured. Since the absorption bands of the HOB are identified as electronic transitions, the change of the absorption coefficient reflects the transformation of the corresponding defect state under illumination. The defect state giving rise to the HOB has been proposed to be located slightly below $E_c - 0.15$ eV [9]. Before illumination, the position of the Fermi level is in the middle of the band gap, and the occupancy of the defect state giving rise to the HOB is too low to be observed. Under illumination, the generation of photoexcited carriers leads to a shift of the quasi-Fermi level towards the conduction band. As a result, the occupancy of the defect state increases, and the absorption becomes detectable. Experimentally, we observe that the most effective energy of the illuminating light at 7 K is in the range of 1.2–1.3 eV, band-edge light, which is in agreement with the results of Corelli and co-workers [7] and Sahu and co-workers [12]. This dependence can be attributed to the characteristics of intrinsic photoexcitation in bulk Si.

In figure 3, we show the time dependence of the photoexcitation (left-hand side) and the decay (right-hand side) of the HOB at 1102 cm^{-1} of the sample annealed for 40 h. The measurement temperature is 7 K, and the illuminating light is 1.23 eV. The ratio of the illuminating-light intensities for curves 1–3 is 1:0.2:0.06; for curve 4 the intensity is the same as that of curve 2, but the illuminating time is only 400 s. It is found experimentally

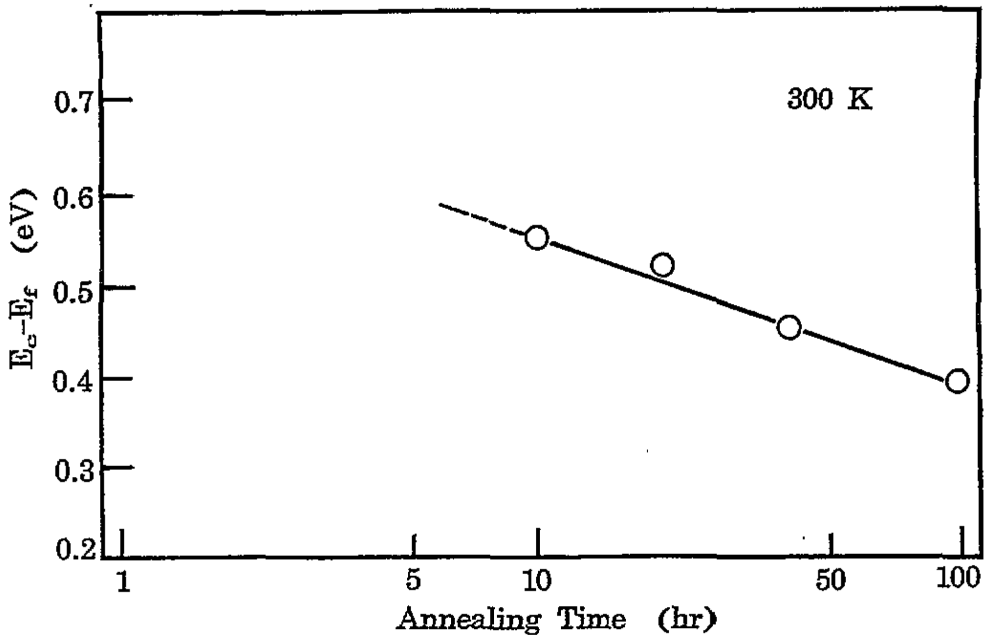

Figure 2. The Fermi-level position at 300 K versus annealing time in the samples annealed at 450 °C.

that the relative absorption coefficients of the prominent bands are almost constant during the photoexcitation and decay. Thus, the band at 1102 cm^{-1} with the highest absorption peak is used as a representative result. After the illuminating light is turned on, the absorption begins to increase and then approaches a saturation value. Owing to the limitation of time resolution, the fast process (< 30 s) is difficult to measure during the photoexcitation and decay. In the process of the photoexcitation for the curves 1–3, the variation of the absorption coefficient α_i can be described by

$$\alpha_i(t) = \alpha_{0i}[1 - \exp(t/\tau_{ei})] \tag{1}$$

where τ_{ei} is the photoexcitation time constant, which is inversely proportional to the illuminating-light intensity, and α_{0i} is the saturation value of the absorption ceofficient. Moreover, the dependence of α_{0i} on the illuminating-light intensity is given in figure 4. It can be seen clearly that the saturation value increases with illumination proportionally to the logarithm of illuminating-light intensity in the range of low light intensities.

When the illuminating light is switched off, the absorption coefficient decays slowly to a residual value rather than the initial value. A very important point is that the absorption coefficients decay to nearly the same residual value, in spite of the differences between their saturation values α_{0i}. Here, this decay behaviour is well fitted by the logarithmic function of time

$$\alpha_i(t) = A_0 \ln[(t + t_{0i})/\tau_d] \tag{2}$$

where τ_d is the decay time constant, and t_{0i} is a parameter also inversely proportional to the illuminating-light intensity. The τ_d in this sample estimated from the present data is

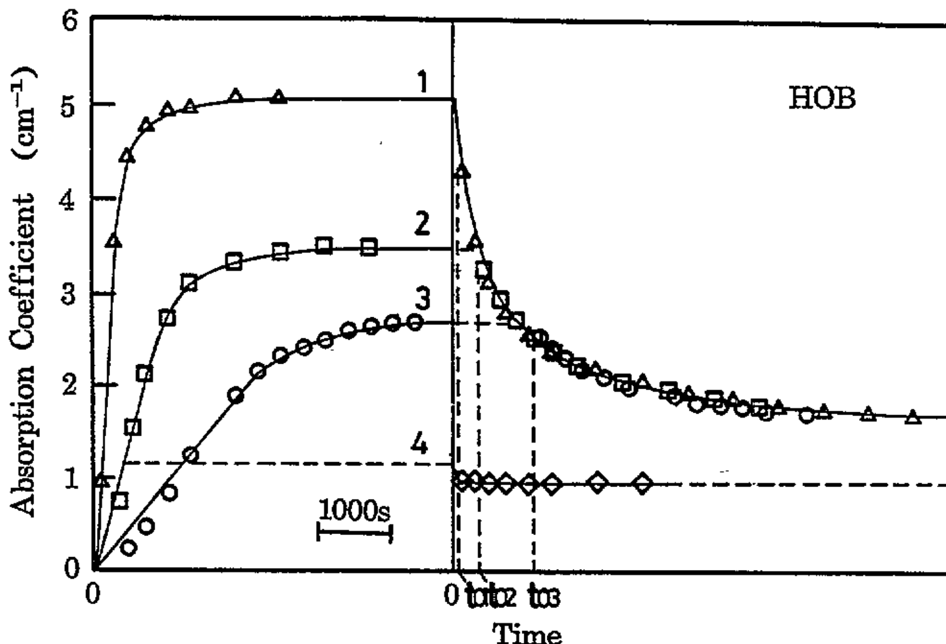

Figure 3. The time dependence of the absorption coefficient of the HOB during photoexcitation (left-hand side) and decay (right-hand side) at 7 K of the sample annealed at 450 °C for 40 h. The solid lines on the left are fitting curves with exponential time functions and those on the right curves with logarithmic functions (see the text).

about 10^5 s at 7 K. Thus, the residual absorption remains practically unchanged during our measurements. Further, if the illumination-induced absorption is lower than the residual value, there is no obvious decay process (see curve 4 in figure 3). It should be pointed out that similar observations are obtained in all present samples.

4. The macroscopic-barrier model

Carrier recombination via defect clusters is analysed on the basis of the macroscopic-barrier model [16, 18, 19]. To avoid complication, the analytic expressions here are limited to discussing that subject as generally as possible without referring to any particular structure of defect clusters in n-type Si. Defect clusters introduced by fast-neutron irradiation are assumed to distribute homogeneously in the matrix. Owing to the traps in a defect cluster, a large number of majority carriers are trapped, and the defect cluster is electrically charged, a spherical space charge of opposite polarity is then formed, creating a potential barrier, as shown in figure 5. This potential barrier spatially dissociates photoexcited carrier pairs: minority carriers are captured by traps, while majority carriers can remain mobile in the defect-free regions. At low temperatures, only a small fraction of the majority carriers will have sufficient energy to overcome the barrier and recombine. This, consequently, results in a slow relaxation of photoexcited carriers.

Under quasi-equilibrium conditions, the carrier recombination rate R_e for electrons via defect clusters with a potential barrier height V_d is expressed approximately by [16, 18]

$$R_e = NN_d[C_n n(1-f)\exp(-qV_d/kT) - E_n f] \tag{3}$$

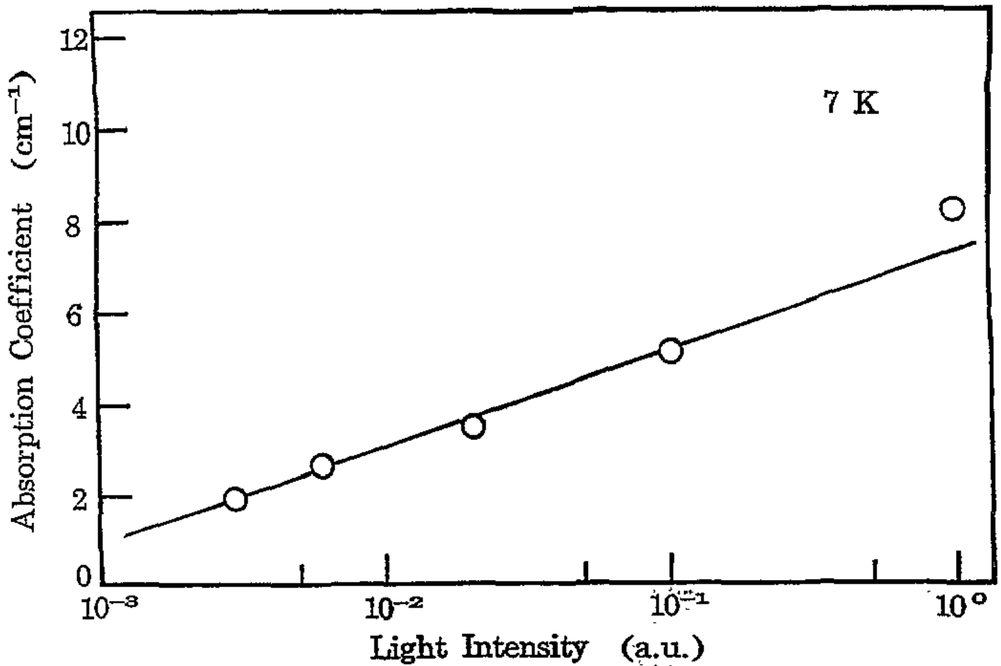

Figure 4. The dependence of the saturation value of the absorption coefficient on the illuminating-light intensity at 7 K in the sample annealed at 450 °C for 40 h.

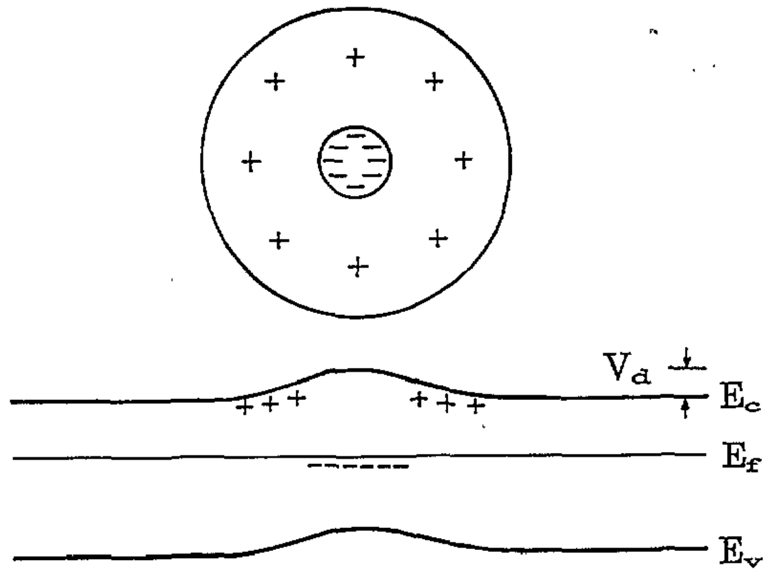

Figure 5. A schematic illustration of the potential barrier for a defect cluster in n-type Si.

where N and N_d are the density of defect clusters and the number of traps in a defect cluster, respectively, f is the occupancy of a trap in the negatively charged state, C_n and E_n are the electron capture and emission rates, n is the electron concentration in the matrix, and q

is the electron charge. Correspondingly, the parameters in equilibrium are denoted with the subscript symbol 0. Δn and Δp are the excess electron concentration and the excess hole concentration, respectively.

The factor η, describing the relative deviation of the occupancy f from the equilibrium value f_0, is defined as

$$\eta = (f_0 - f)/f_0. \tag{4}$$

For the sake of simplicity, within a limited range of variation, V_d can be assumed to be proportional to f, namely, $V_d \sim V_{d0} f/f_0$. From charge neutrality and $\Delta n \gg \Delta p$, one obtains

$$\Delta n = f_0 N N_d \eta. \tag{5}$$

Hence, equation (3) can be rearranged as

$$R_e = C_n n_0 N N_d (1 - f_0) \exp[-\beta V_{d0}(1 - \eta)] \times \left\{1 - \exp(-\beta V_{d0}\eta) + \eta \left[\frac{f_0}{1 - f_0} + \exp(-\beta V_{d0}\eta)\right]\right\} \tag{6}$$

where $\beta = q/kT$.

At low temperatures, one can simplify further for $\beta V_d \eta \gg 1$:

$$R_e = C_n n_0 N N_d (1 - f_0) \exp(-\beta V_{d0}) \exp(\beta V_{d0}\eta). \tag{7}$$

We consider the condition where electron–hole pairs are homogeneously generated at a rate G. At steady state $R_e = G$, the saturation value of the excess electron concentration $\Delta n(\infty)$ is given by

$$\Delta n(\infty) = (f_0 N N_d/\beta V_{d0})[\ln G + \ln[\exp(\beta V_{d0})/C_n n_0 N N_d (1 - f_0)]]. \tag{8}$$

It should be noted that $\Delta n(\infty)$ is proportional to the logarithm of the generation rate G. This relation is valid within the range of low light intensities.

Now let us assume that the illumination is switched off at the moment $t = 0$, and the excess carriers decay in time. The time dependence of $\Delta n(t)$ can be described by

$$\Delta n(t) = (f_0 N N_d/\beta V_{d0}) \ln((t + t_0)/\tau_d) \tag{9}$$

where

$$\tau_d = [f_0/(1 - f_0) C_n n_0/\beta V_{d0}] \exp(\beta V_{d0})$$

and

$$t_0 = (f_0 N N_d/\beta V_{d0})/G.$$

Here t_0 is a parameter that is inversely proportional to the light intensity, and τ_d is the decay time constant. The analytic expressions presented here indicate an essentially logarithmic time decay of photoexcited carriers. This is the most important feature for the macroscopic barrier model, distinguishing it from other models. For the photoexcitation process, not discussed here, Δn can be described by an essentially exponential time dependence. It should be remembered that our experimental conditions do satisfy the requirements for the approximations in the above analytic expressions.

5. Discussion

It has been noted that our observations are very similar to the main features of the analytic expressions derived above. An important question is, therefore, whether the variations of the absorption coefficient are associated with the slow relaxation of photoexcited carriers or whether those similarities are only accidential. Here, we shall further discuss the property of the photoexcitation and decay of the HOB.

Slow relaxation phenomena of defect states after optical excitation have been investigated intensively in Si and compound semiconductors, which usually involves metastable properties. So far, thre is no appropriate model concerning metastable defect states that could be used to interpret the present observations, especially the decay process following a logarithmic time dependence. From our point of view, whether a theoretical model can thoroughly explain the observations greatly depends on whether or not it can successfully describe the decay behaviour. It is unrealistic to attribute several lifetimes to force fit the decay by assuming different physical mechanisms. On the other hand, in order to explain the residual absorption of the HOB, Corelli and co-workers proposed that the defect related to the HOB has three charge states, in which the intermediate state is a very strong electron trap that captures photoexcited electrons at low temperatures [7]. However, this model is not able to explain our detailed experimental results. Moreover, differences in the photoexcitation and decay of the HOB, for example, the decay time constant among the samples having undergone different irradiation or annealing conditions, have been observed. This implies that the behaviour of the photoexcitation and the decay of the HOB is not governed mainly by the defect itself.

One of the main features for fast-neutron radiation is the introduction of defect clusters. The change of electrical parameters could be characterized by the presence of fast-neutron-radiation-induced defect clusters in an initial high-resistivity Si annealed below 600 °C [20, 21]. Defects, such as dislocation loops, voids, and rod-like defects, have been observed by electron microscopy in neutron irradiated silicon annealed at temperatures between 400 ∼ 500 °C [22, 23]. In the present samples, cluster-like defects were detected with the electron-dipole-spin-resonance method [24]. These defects are able to play a 'potential-barrier' role and result in the slow relaxation of photoexcited carriers at low temperatures [13].

The absorption bands of the HOB have been identified as electronic transitions, and the defect state giving rise to the HOB was proposed to be located slightly below $E_c - 0.15$ eV in the band gap. Within the range considered, the quasi-Fermi level being located between the defect level and the Fermi level in the present samples, the occupancy of the defect state can be assumed to be proportional to the excess electron concentration Δn. Consequently, the variation of the absorption coefficient α reflects that of Δn. Further important evidence is obtained from fast-neutron-irradiated Czochralski Si, where the similarities for the photoexcitation and decay of the absorptions between the HOB and the thermal-donor single-ionized state TD^+ have been observed [9]. This supports the idea that the photoexcitation and decay of the HOB are associated with the relaxation of photoexcited carriers.

6. Conclusion

From the present investigation on the optically active process of the HOBs in fast-neutron-irradiated Fz-Si, it is found that the photoexcitation process follows an exponential time dependence and that the decay follows a logarithmic time dependence with a decay time

constant of 10^5 s at 7 K. The saturation value of the absorption coefficient depends on the logarithm of the illumination-light intensity at low light intensities. Analytic expressions for the relaxation process of photoexcited carriers are derived with the macroscopic-barrier model, which is in good agreement with the observations. The photoexcitation and decay of the HOB are associated with the slow relaxation of photoexcited carriers, resulting mainly from the presence of defect clusters.

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