Transformation of divacancies to divacancy-oxygen pairs in p-type Czochralski-silicon; mechanism of divacancy diffusion

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In this work, a comprehensive study on the transition of divacancy (V_2) to divacancy-oxygen (V_2O) pairs in p-type silicon has been performed with deep level transient spectroscopy (DLTS). Czochralski grown, boron doped p-type, silicon samples, with a doping concentration of 2×10^{15} cm^{-3} and oxygen content of $7.0 \pm 1.5 \times 10^{17}$ cm^{-3}, have been irradiated with 1.8 MeV protons. Isothermal annealing at temperatures in the range of 200 °C–300 °C shows a close to one-to-one correlation between the loss in the donor state of V_2 and the formation of the donor state of V_2O, located at 0.23 eV above the valence band edge. A concurrent transition takes place between the single acceptor states of V_2 and V_2O, as unveiled by injection of electrons through optical excitation during the trap filling sequence of the DLTS measurements. Applying the theory for diffusion limited reactions, the diffusivity of V_2 in the studied p-type samples is determined to be $(1.5 \pm 0.7) \times 10^{-3}\exp[-(1.31 \pm 0.03) \text{ eV}/kT]$ cm^2/s, and this represents the neutral charge state of V_2. Further, the data seem to favor a two-stage diffusion mechanism involving partial dissociation of V_2, although a one-stage process cannot be fully excluded. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4862435]

I. INTRODUCTION

The divacancy (V_2) is one of the most fundamental defects in Si stable at room temperature (RT) and can greatly influence the electrical and optical properties of Si-based devices.[1,2] V_2 has four charge states: Positive, neutral, singly negative, and doubly negative.[3] Levels observed by Deep Level Transient Spectroscopy (DLTS) at about $E_v + 0.19$ eV, $E_c - 0.43$ eV, and $E_c - 0.23$ eV are attributed to positive (+/0), negative (−/0) and doubly negative (=/−) transitions of V_2, respectively, where E_v and E_c denote the valence and conduction band edge, respectively.

The concentration of V_2 is strongly enhanced after particle irradiation and/or ion implantation, and V_2 is stable up to temperatures around 200 °C. In an early study using electron paramagnetic resonance (EPR) measurements,[4] it was found that V_2 starts to migrate above 200 °C with an activation energy (E_a) of ≈1.3 eV. The study suggested that V_2 is more stable in Float zone (FZ) Si, as compared to Czochralski (Cz) Si, due to the lower impurity (trap) content. In FZ-Si, dissociation was suggested to be the main annealing mechanism with an activation energy of 1.9 eV to break up V_2. One of the most abundant impurities in Cz-Si is interstitial oxygen (O_i) which is present at concentrations of 10^{17}–10^{18} cm^{-3}. V_2's are trapped by O_i, and the divacancy oxygen interaction is normally the main mechanism of the V_2 annealing in irradiated Cz-Si.[3]

The divacancy-oxygen (V_2O) complex was first observed in an EPR study of heavily electron irradiated Cz-samples.[3] Later, a vibrational band at 833.5 cm^{-1} in infra-red absorption spectra was ascribed to V_2O.[5] This was further supported by positron annihilation spectroscopy studies in which an increase in the V_2O concentration was observed after the annealing of V_2.[6] Theoretical studies of the V_2O complex have predicted one donor and two acceptor levels in the energy band gap.[7,8] In an early DLTS study of irradiation induced defects in high purity, n-type, oxygen-enriched FZ (DOFZ) Si, a gradual shift in the position of the $V_2(=/−)$ and $V_2(−/0)$ peaks was observed after heat treatments at ~200–250 °C.[9,10] This shift was attributed to annealing of V_2 and formation of a new center with two levels at $E_c - 0.24$ eV and $E_c - 0.46$ eV. These new levels have similar electronic properties to those of $V_2(=/−)$ and $V_2(−/0)$ and were tentatively identified as the single and double acceptor states of V_2O. Further, it was found that the shift in the level positions occurs faster in material with high oxygen content, and the growth of the new levels showed a one-to-one proportionality with the loss of V_2. The detailed formation kinetics of the $E_c - 0.24$ eV and $E_c - 0.46$ eV states was studied by Mikelsen *et al.*,[11] and the two states could now more firmly be assigned to V_2O, as also supported by theory.[8] Moreover, quantitative values for the diffusivity of V_2 were deduced in Ref. 11 by modelling of the experimental data for the reaction kinetics, and an activation energy of 1.30 ± 0.02 eV with a pre-exponential factor of $(3 \pm 1.5) \times 10^{-3}$ cm^2/s was obtained for the migration of V_2 in low to moderately doped n-type samples.

In p-type material, however, the detailed kinetics of the transformation of $V_2(+/0)$ has not been studied quantitatively. Trauwaert *et al.*[12] observed a shift in the position of the $V_2(+/0)$ level to $E_v + 0.24$ eV in annealed electron irradiated p-type material using both Cz and FZ samples. The shift occurs faster in the Cz samples, and it was proposed that the new level is related to $V_2O(+/0)$. In a recent study by

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Markevich *et al.*,[13] a similar shift of the $V_2(+/0)$ peak was observed, and it was discussed that the emerging level is a combination of $V_2O(+/0)$ and a donor state of the trivacancy-oxygen center, $V_3O(+/0)$. In Ref. 14, the transformation of $V_2(+/0)$ to the $E_v + 0.24$ eV level was found to have a one-to-one proportionality in Cz-samples, yielding strong evidence for the assignment of the $E_v + 0.24$ eV level to $V_2O(+/0)$. In addition, in Ref. 14, the growth of the $E_v + 0.24$ eV level was shown to occur simultaneously with that of the $V_2O(-/0)$ level by combining results from DLTS and optically-induced minority carrier transient spectroscopy (MCTS) (so-called ODLTS) measurements on the same samples.

Accordingly, the transformation of V_2 to V_2O can be regarded as well-established with distinct levels for both centers, and by studying the detailed transformation kinetics in both p-type and n-type samples with a known concentration of O_i, the atomic mechanism(s) of V_2 diffusion can be unveiled. Watkins and Corbett demonstrated that V_2 could diffuse large distances prior to dissociation. It has usually been assumed that the diffusion occurs via a two-stage process, where the two adjacent vacancies have to separate one lattice spacing and then recapture, i.e., via partial dissociation.[4] Later, in theoretical results by Hwang and Goddard,[15] it was found that no sizable barrier exists for stabilizing the partially dissociated (V-Si-V) configuration. It was predicted, thus, that V_2 migrates via one-stage hopping of a Si atom along the divacancy with a saddle point in the V-Si-V configuration. Calculations have also suggested that the total energy difference between the V-V and V-Si-V states is 1.36 eV. Since the V-Si-V configuration is unstable, a full dissociation process requires two Si atoms to move simultaneously between the two monovacancies.[15]

In the present work, we report on detailed annealing kinetics studies of V_2 and the transformation to V_2O in boron doped, p-type Cz-Si samples. The activation energy and the pre-exponential factor for V_2 migration have been deduced and by comparison with corresponding data for moderately doped n-type samples, compiled from the literature, the detailed atomic mechanism for migration of neutral V_2 centers is discussed. These data tend to favor a mechanism involving partial dissociation of V_2 rather than a one-stage hopping process.

II. EXPERIMENTAL

The samples studied were n^+p diodes fabricated using Cz-Si wafers with a resistivity of ~6 Ω-cm. First, the wafers were dry oxidized at 1100 °C for 3 h to grow a 250 nm thick SiO_2 layer. Standard positive photolithography and wet etching using buffered oxide etch (BOE) were then applied to open holes with a diameter of 200–2000 μm in selected areas. The n^+-layer was formed by in-diffusion of phosphorous (P) from gas phase in a quartz tube. Aluminum Ohmic contacts were prepared by thermal evaporation on the front side (n^+-side) and silver paste was used as the contact on the backside after removal of the SiO_2 layers by BOE. The oxygen, [O], and carbon, [C], concentration in the samples were

$7.0 \pm 1.5 \times 10^{17}$ cm^{-2} and $\leq 2 \times 10^{16}$ cm^{-3}, respectively, as determined by secondary ion mass spectrometry (SIMS).

Irradiation of the diodes was performed at RT with 1.8 MeV protons to a dose of 2×10^{12} cm^{-2}; the projected range of the protons was ~40 μm, as estimated by simulations using the TRIM code, and far beyond the extension of the region probed by the DLTS (ODLTS) measurements (~1 μm). Prior to the DLTS measurements, the samples were pre-annealed for 20 min at 200 °C in order to remove minor, unstable defects which are not relevant in this study. Isothermal annealing was carried out at five different temperatures (200 °C, 225 °C, 250 °C, 275 °C, and 300 °C). During the annealing, out-diffusion of H from the region around the projected range may be anticipated, but no indications of H-related levels were found in the DLTS/ODLTS spectra.

The DLTS measurements were carried out by employing a refined version of the set up described in Ref. 16. The reverse bias voltage was kept at 10 V and the filling pulse voltage was -10 V with a duration of 50 ms. The temperature was scanned between 40 and 300 K. ODLTS was employed using a light emitting diode for the optical excitation with a pulse duration of 200 ms, wavelength of 940 nm, and power of 4 mW. The illumination was done from the back side of the samples and the reverse bias was kept at 10 V. A high resolution weighting function (GS4)[17] was applied for the extraction of DLTS spectra from the recorded capacitance transients and a lock-in weighting function for the ODLTS spectra.

III. RESULTS AND DISCUSSION

Figure 1 shows DLTS and ODLTS spectra of irradiated samples after pre-annealing and isothermal annealing at 300 °C. The DLTS spectrum reveals three major peaks after the pre-annealing at 200 °C for 20 min; these levels are identified, in accordance with the literature, as the single donor state
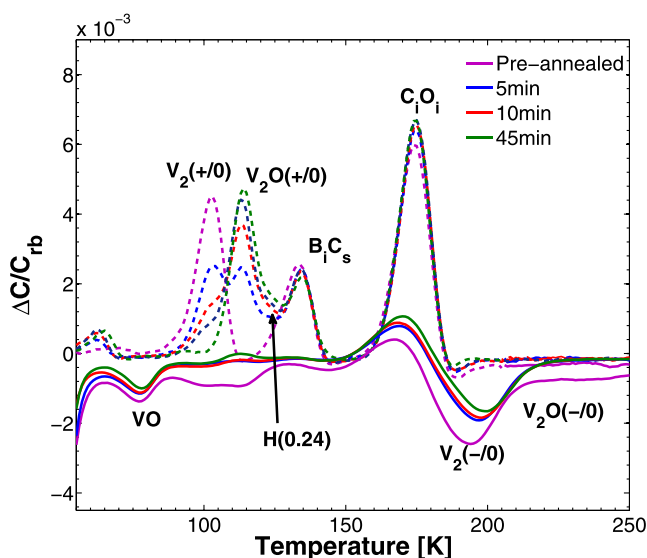

FIG. 1. DLTS (dashed lines) and ODLTS (solid lines) spectra of proton irradiated samples after pre-annealing (200 °C/20 min) and isothermal annealing at 300 °C for different durations. The rate window used is (640 ms)$^{-1}$, and the weighting functions are GS4 and "lock-in" for DLTS and ODLTS, respectively.
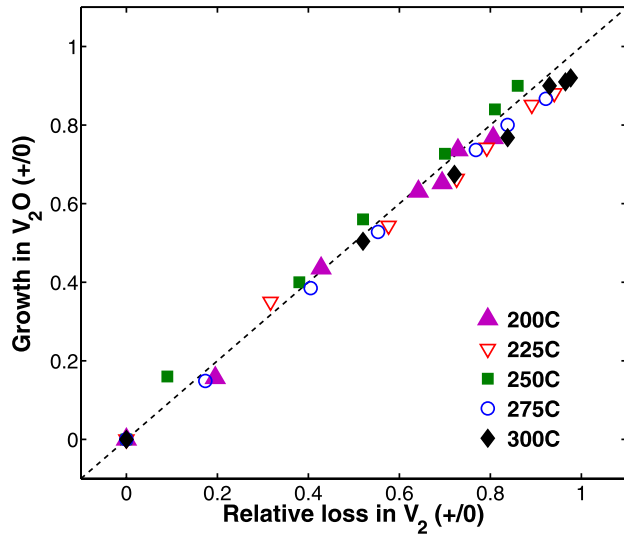
FIG. 2. Growth in V_2O amplitude, normalized to the initial amplitude of V_2, versus the relative loss in V_2 amplitude during isothermal annealing. The dotted line represents a one-to-one proportionality between V_2O growth and V_2 loss.

of the divacancy ($V_2(+/0)$), interstitial boron–substitutional carbon (B_iC_s)[18] and interstitial carbon–interstitial oxygen (C_iO_i)[19] with energy level positions at $E_v + 0.19\,eV$, $E_v + 0.29\,eV$, and $E_v + 0.36\,eV$, respectively. The ODLTS analysis reveals two clear electron traps with positions at $E_c - 0.18\,eV$ and $E_c - 0.44\,eV$ that are identified as the vacancy oxygen pair (VO)[20] and $V_2(-/0)$, respectively.

During the isothermal annealing, a gradual decrease in the $V_2(+/0)$ level is observed, and a new level appears at $E_v + 0.23\,eV$ with an apparent hole capture cross section of $\sim 10^{-15}$ cm^2. The increase in the amplitude of the $E_v + 0.23\,eV$ level, assigned to $V_2O(+/0)$,[12–14] exhibits a close one-to-one correlation with the loss of $V_2(+/0)$ (Fig. 2). In addition, a minor defect level H(0.24) with a position at $E_v + 0.24\,eV$ can also be resolved. The formation of H(0.24) exhibits similar behavior to that of $V_2O(+/0)$ and a possible identification as $V_3O(+/0)$ has been put forward.[13,21]

Similar to $V_2(+/0)$ and in accordance to previous studies, annealing of the $V_2(-/0)$ peak is observed in the ODLTS spectra (Fig. 1) after the isothermal heat treatments, and a new level, assigned to $V_2O(-/0)$, occurs at $E_c - 0.46\,eV$. Here, it should be pointed out that the amplitudes of the $V_2 (+/0)$ and $V_2 (-/0)$ peaks are not equal. Variation of the optical pulse duration during the ODLTS measurements showed that the amplitude of the $V_2(-/0)$ signal saturated for pulses >100 ms without reaching the full strength of $V_2 (+/0)$. This incomplete filling of $V_2(-/0)$ can be explained by a balance between the capture rate of optically excited electrons and the emission of the captured electrons. Under the present conditions, the capture, displaying a saturation time of 100 ms, is limited by the excitation power and the proton-induced peak damage in the bulk of the samples ($\sim 40\,\mu m$), which suppresses the amount of the excited electrons that can reach the probing region of ODLTS from the illuminated back side. Accordingly, the capture rate becomes slow and comparable with the emission rate at the temperatures where the $V_2(-/0)$ peak occurs.

Fig. 3(a) shows the amplitude of $V_2(+/0)$ as a function of annealing time, t, and the annealing can be described by first order kinetics

$$[V_2] = [V_2]_{t=0}\,e^{-c(T)t}, \tag{1}$$

where c(T) is the temperature dependent rate constant and $[V_2]$ is the concentration of V_2. In Fig. 3(b), the relative difference between $[V_2(+/0)]_{t=0}$ and $[V_2O(+/0)]$ is shown versus annealing time for all the temperatures studied. The growth of the $V_2O(+/0)$ can be described by the relation

$$[V_2O] = [V_2]_{t=0} - [V_2]_{t=0}\,e^{-c(T)t}, \tag{2}$$

where $[V_2O]$ is the concentration of V_2O.

Fig. 4 shows the Arrhenius plot of c(T) for both the annealing of V_2 and the growth of V_2O, where c(T) exhibits a thermally activated behavior
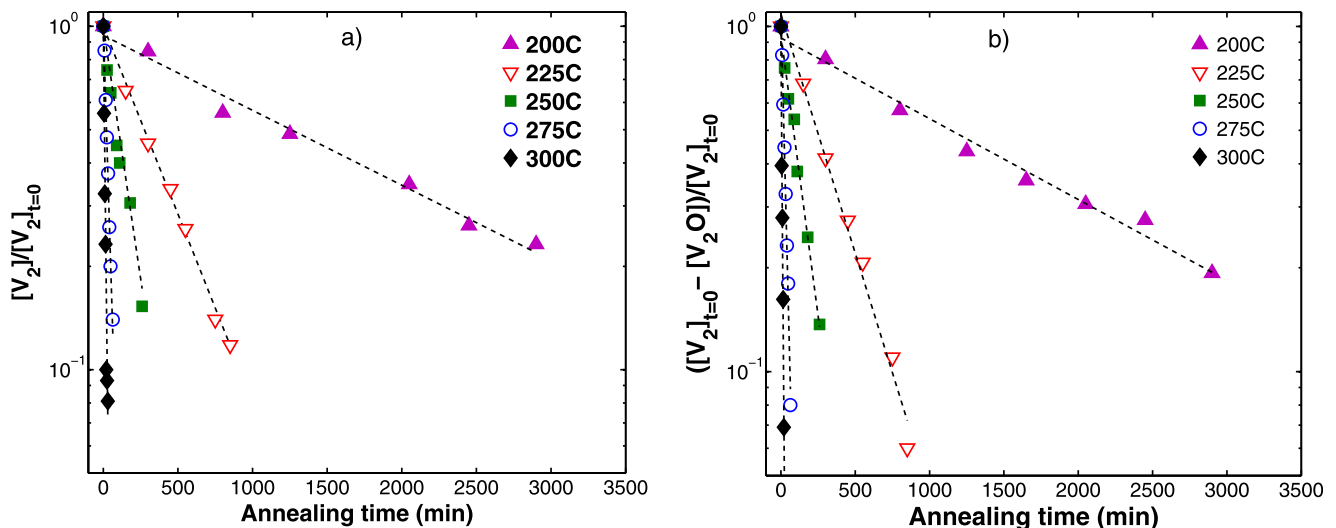

FIG. 3. Loss of $V_2(+/0)$ (a) and the difference between the initial concentration of V_2 (+/0) and the growing concentration of $V_2O(+/0)$ (b) during isothermal annealing at 200, 225, 250, 275, and 300 °C. The values have been normalized to the initial amplitude of V_2. The dotted lines represent least squares exponential fits to the experimental data.
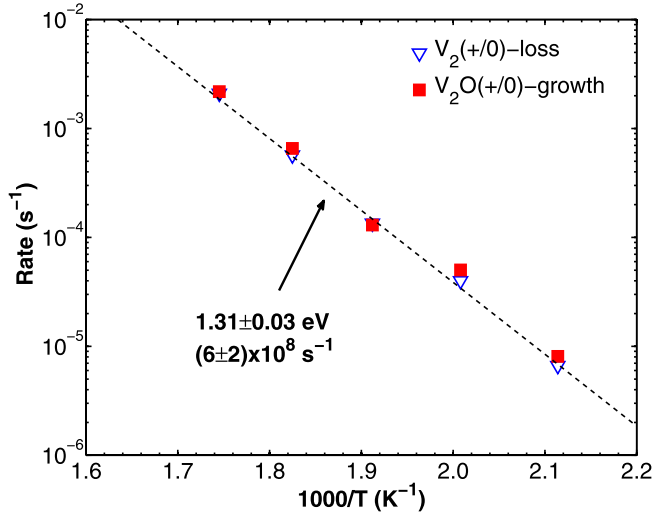
FIG. 4. Arrhenius plot for the annealing and formation rates of V_2 and V_2O, respectively. The dotted line represents an exponential fit of the rate values.

$$c(T) = c_0 e^{-\frac{E_a}{kT}}, \qquad (3)$$

where E_a is the activation energy and c_0 is the frequency factor. Both rates are closely described by $E_a = 1.31 \pm 0.03$ eV and $c_0 = (6 \pm 2) \times 10^8$ s^{-1}. The value deduced for E_a is practically identical to that obtained for n-type material by Mikelsen *et al.*[11] and reflects that V_2 is in the same charge state (neutral) in both the experiments. Indeed, in both Ref. 11 and in the present experiments, the Fermi level at the investigated temperatures (200–300 °C) is below the $V_2(-/0)$ transition at $E_c - 0.43$ eV and above the $V_2(+/0)$ transition at $E_v + 0.19$ eV. This results in neutral charge state of V_2 in both cases.

The diffusivity of V_2, D_{V2}, can be quantitatively estimated from the results in Fig. 4. Applying the theory for diffusion limited reactions,[22] the following reactions for V_2 and V_2O hold:

$$\frac{d[V_2(t)]}{dt} = -c(T)[V_2(t)] = -4\pi R D_{V2}[O_i][V_2(t)], \qquad (4)$$

$$\frac{d[V_2O(t)]}{dt} = -\frac{d[V_2(t)]}{dt} = 4\pi R D_{V2}[O_i][V_2(t)], \qquad (5)$$

where R is the capture radius for the trapping reaction and $[O_i]$ is the concentration of interstitial oxygen. In Eq. (4), O_i is assumed to be immobile exhibiting a diffusivity of $<10^{-23}$ cm^2/s in the studied temperature range.[23] By combining Eqs. (3) and (4) with $D_{V2} = D_{V2}^0 e^{-\frac{E_a}{kT}}$ one obtains

$$D_{V2}^0 = \frac{c_0}{4\pi R[O_i]}. \qquad (6)$$

Putting R equal to 5 ± 1 Å, $[O_i]$ to $7 \pm 1.5 \times 10^{17}$ cm^{-3}, and using $c_0 = (6 \pm 2) \times 10^8$ s^{-1}, one gets $D_{V2}^0 = (1.5 \pm 0.7) \times 10^{-3}$ cm^2/s. This value is within the experimental accuracy equal to $(3 \pm 1.5) \times 10^{-3}$ cm^2/s determined previously for lightly and moderately doped n-type material.[11] In Fig. 5, the absolute values extracted for D_{V2} are depicted versus the
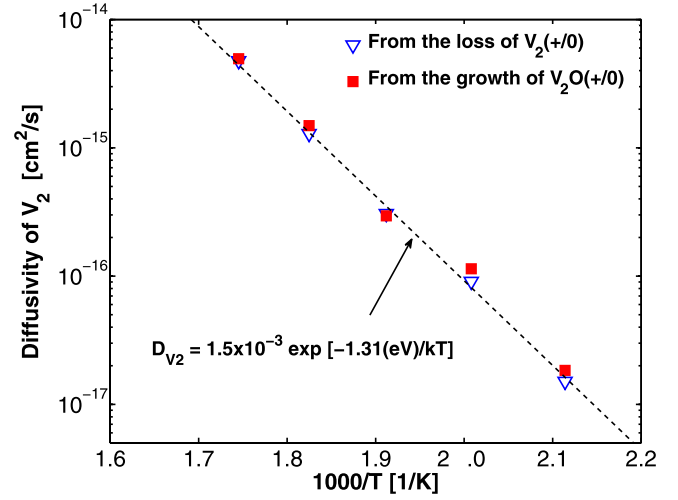

FIG. 5. The temperature dependence of the diffusion coefficient for V_2.

reciprocal absolute temperature and they are described by $(1.5 \pm 0.7) \times 10^{-3} \exp[-(1.31 \pm 0.03)$ eV/kT].

D_{V2} can be described theoretically using the following expression:[24]

$$D_{V2} = ga^2 \nu e^{-\frac{\Delta S}{k}} e^{-\frac{E_a}{kT}}, \qquad (7)$$

where g is a geometrical factor, a is the lattice constant, ν is the attempt frequency, and ΔS is the entropy change. The divacancy can not migrate simply by a single jump of one atom into an adjacent vacant site; either a jump of an atom over a next-neighbor distance (one-stage process) or a partial dissociation (two-stage process) must be involved. According to Swalin,[24] these two mechanisms have a direct impact on the geometrical factor: g = 1/8 for the one-stage process (direct jump) and g = 1/32 for the two-stage process with partial dissociation. Assuming the frequency factor to be equal to the Debye frequency in Si $\nu = 1.3 \times 10^{13}$ Hz[24] and $\exp(-\Delta S/k) \approx 1$, the theoretical estimate for D_{V2}^0 is 4.8×10^{-3} cm^2/s and 1.2×10^{-3} cm^2/s for the one-stage and two-stage processes, respectively. Comparing these theoretical estimates for D_{V2}^0 with the value extracted from the experimental data, it is tempting to conclude that the experiment supports the mechanism with partial dissociation as the dominant for migration of V_2 in the neutral charge state. On the other hand, the theoretical values assume the attempt frequency equal to the Debye frequency and the entropy factor equal to unity, which can significantly overestimate D_{V2}^0.

IV. CONCLUSIONS

Isothermal annealing studies of V_2 in proton irradiated p-type, Cz-Si samples have been performed in the temperature range of 200–300 °C. A simultaneous transition of $V_2(+/0)$ and $V_2(-/0)$ to the corresponding states of V_2O is demonstrated using DLTS and ODLTS, respectively. The transition exhibits first order kinetics with a close one-to-one proportionality, and the rate is thermally activated with an energy of 1.31 ± 0.03 eV. Within the experimental accuracy, V_2 and V_2O show an identical annealing and growth behavior, respectively, as in moderately and lightly doped n-type

oxygen-rich materials. In both the p-type and n-type materials, V_2 appears in the neutral charge state during the transformation to V_2O, and the identical behavior reflects the diffusion of neutral V_2's. Applying the theory for diffusion limited reactions, the diffusivity of V_2 has been extracted and is given by $(1.5 \pm 0.7) \times 10^{-3} \exp[-(1.31 \pm 0.03)$ eV/kT] cm^2/s. Comparison with first-order theoretical estimates of V_2 migration shows good agreement and seems to favor partial dissociation of V_2 as the prevailing diffusion mechanism, rather than a one-stage process. However, further studies are required before a more definite conclusion can be made.

ACKNOWLEDGMENTS

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