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Divacancy annealing in Si: Influence of hydrogen

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We have performed comparative studies of divacancy (V_2) annealing in hydrogenated and nonhydrogenated Si by deep level transient spectroscopy. It is shown that the nonhydrogenated samples demonstrate the formation of divacancy-oxygen (V_2O) complex during annealing of V_2, while the hydrogenated samples demonstrate annealing of V_2 without correlated growth of electrically active centers. No substantial formation of divacancy-hydrogen (V_2H) complexes is observed in the hydrogenated samples. It is suggested that the dominant mechanism of V_2 annealing in hydrogen-rich Si is the interaction with hydrogen molecules (H_2) that results in the formation of the V_2H_2 complex.

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The discussion on the mechanisms of impurity-assisted annealing of divacancy (V_2) in Si has attracted a renewed interest. This is due to recent reports on the observation of a double acceptor center identified as the divacancy-oxygen center (V_2O).[1–3] These reports have considerably improved the understanding of the mechanisms of V_2 annealing and, at the same time, raised new questions concerning the origin of the dominant mechanism.

From the first experimental observations of V_2 by electron paramagnetic resonance (EPR), it has been established that V_2 is more stable in float-zone (FZ) Si as compared to Czochralski (Cz) Si.[4] This difference has been explained by assuming the existence of two competing mechanisms: (i) the dissociation of V_2 and (ii) the migration of V_2 with subsequent annihilation/passivation at an impurity trap. It has been estimated that the V_2 dissociation has an activation energy of ~1.6 eV and the V_2 migration has an activation energy of ~1.3 eV. Since FZ-Si contains relatively small amounts of the impurity traps, most of the V_2's are stable up to the temperature of dissociation. In contrast, Cz-Si is known to contain relatively high concentrations of impurities, and most of the V_2's can be annealed by the migration mechanism with lower activation energy. It has been found in further studies that a fraction of the V_2's can anneal in Cz-Si by interacting with interstitial oxygen (O_i), forming V_2O.[5]

A different situation can be observed in studies of the V_2 annealing by electrical characterization techniques such as deep level transient spectroscopy (DLTS). The thermal stability of V_2 in FZ-Si has been found to be higher than that in Cz-Si, in accordance with the EPR results. However, in contrast to EPR, the DLTS studies have yielded almost identical values of the activation energy for the V_2 annealing in FZ-Si and Cz-Si (with a lower annealing rate by a factor of ~2 in FZ-Si due to a smaller pre-exponential factor), which favors the migration mechanism in both of the materials.[6] It has also been established (see Ref. 6 and references therein) that the annealing of V_2 in both FZ- and Cz-Si does not result in the formation of electrically active centers. These observations exclude the interaction $V_2+O_i \rightarrow V_2O$ as a dominant mechanism since the oxygen content is at least an order of magnitude higher in Cz-Si than in FZ-Si, and V_2O is expected to be electrically active with three electronic levels in the band gap.[7–9]

The discrepancy between the observations by EPR and DLTS can be explained by taking into account that DLTS is applicable to investigations of low concentration of defects (only a few percent of the doping concentration), which is normally well below the concentration of main impurities like oxygen and carbon. Thus, no effect of impurity depletion by interaction with the defects will occur. In contrast, such techniques as infrared absorption and EPR monitor a high concentration of defects, comparable to or above that of most impurities. In this case, the balance of different interactions is affected by the depletion of impurities.

The reports on formation of V_2O during annealing of V_2, observed in high-purity oxygenated FZ-Si by DLTS, have confirmed that the interaction $V_2+O_i \rightarrow V_2O$, where the V_2's are the migrating species, is indeed a possible channel for the impurity-assisted annealing of V_2.[1,2] Recently, an observation of V_2O formation has also been reported in carbon-lean Cz-Si with a typical oxygen concentration of 10^{18} cm^{-3} and presumably low concentrations of other impurities.[3] These reports have raised the question of why such a transformation has not been observed previously in "ordinary" FZ- and Cz-Si. Two possible suggestions can be made. First, the interaction $V_2+O_i \rightarrow V_2O$ has an energy barrier, and an interaction with another unidentified impurity in ordinary FZ-Si and Cz-Si becomes more probable. This suggestion, however, is not supported by *ab initio* calculations where no barrier is observed for the interaction $V_2+O_i \rightarrow V_2O$.[9] Second, it is possible that ordinary FZ-Si and Cz-Si contain considerable concentrations of migrating species that interact with V_2 before it becomes mobile.

In this paper, we have performed comparative studies of high-purity oxygenated Si with and without intentionally introduced hydrogen. It is shown that the nonhydrogenated samples demonstrate the transition of V_2 to V_2O, in accordance with previous results, while the hydrogenated samples reveal annealing of V_2 without correlated formation of V_2O or other electrically active centers. These results imply that the interaction of V_2 with diffusing hydrogen-related species, presumably hydrogen molecules (H_2), can be a dominant

TABLE I. Survey of the samples used in the study.

Sample	Doping, P/cm^3	Oxidation	Oxygenation	Hydrogenation
A	5×10^{12}	21 h dry at 1200 °C	80 h in N_2 at 1150 °C	—
B	5×10^{12}	21 h dry at 1200 °C	80 h in N_2 at 1150 °C	2 h in H plasma at 300 °C

channel for impurity assisted annealing of V_2.

p^+-n^--n^+ diodes were made using high-resistivity and high purity FZ-Si wafers. As a part of the fabrication process, the wafers were oxidized in a dry oxygen atmosphere at 1200 °C for 21 h. Subsequently, the wafers received a so-called oxygenation treatment. Oxygen was diffused into the wafer from the pre-formed silicon dioxide layer at the surface. The oxygenation was performed at 1150 °C in a nitrogen atmosphere for 80 h. An ordinary silicon diode process with boron and phosphorus implantation and post-annealing was then performed. The oxygen and carbon concentrations in the region of DLTS measurements, as determined by secondary ion mass spectrometry, are $(2-3)\times10^{17}$ and $\leqslant 10^{16}$ cm^{-3}, respectively.

Some of the samples were then hydrogenated. The hydrogenation was performed using an OXFORD Plasmalab microwave system, exposing the back n^+ side of the samples to a hydrogen plasma at a pressure of 700 mTorr and a temperature of 300 °C for 2 h. This treatment results in formation of a hydrogen rich layer with a thickness of 0.5 μm and a hydrogen content of $\sim10^{20}$ cm^{-3} near the exposed surface.[10] However, the concentration of hydrogen near the front p^+ side of the diodes (~200–300 μm from the exposed surface), where the DLTS measurements take place, is expected to be substantially lower and not to exceed 10^{17} cm^{-3}. A survey of the samples used in the study is presented in Table I.

The diodes were irradiated at room temperature with 15-MeV electrons and doses of 2×10^{12} and 4×10^{12} cm^{-2}. Subsequently, DLTS measurements were performed, using a setup described elsewhere.[11] In short, the temperature of the sample was scanned between 77 and 280 K, and the measured capacitance transients were averaged in intervals of a width of 1 K. The DLTS signal was extracted by using a lock-in type of weighting function, and different spectra were obtained with rate windows in the range of $(20\text{ ms})^{-1}$ to $(2.56\text{ s})^{-1}$ from a single temperature scan. Concentration, energy level and capture cross section of the traps were then evaluated from the spectra.

For both samples *A* and *B*, DLTS spectra of as-irradiated diodes show the presence of three major peaks with activation enthalpies of 0.43, 0.23, and 0.18 eV that are primarily identified as the singly negative divacancy $V_2(-/0)$, the doubly negative divacancy $V_2(=/-)$ and the vacancy-oxygen (VO) pair, respectively (Refs. 1 and 2 and references therein). The concentration of VO and V_2, as determined by DLTS, is 1.2×10^{11} and 3×10^{10} cm^{-3} for a dose of 2×10^{12} cm^{-2}, and 2.3×10^{11} and 6×10^{10} cm^{-3} for a dose of 4×10^{12} cm^{-2}, respectively. The $V_2(-/0)$ peak contains an overlapping minor contribution from other less stable centers that can be annealed out at 200 °C.[1]

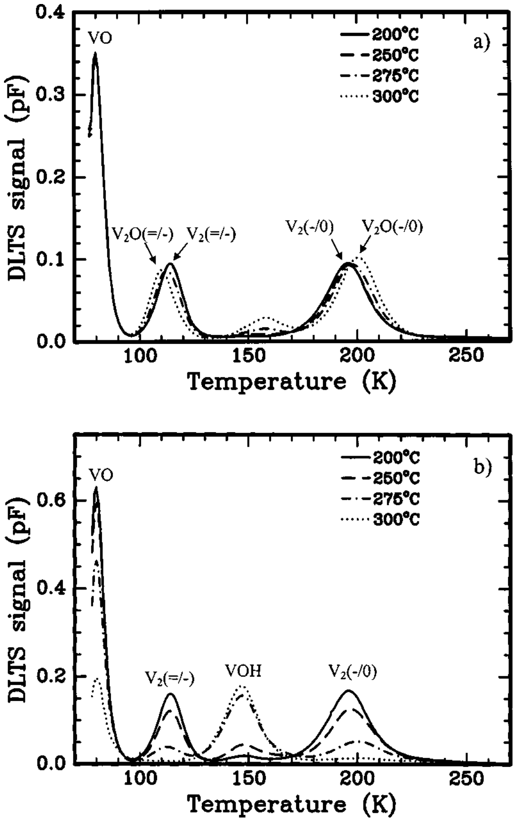

FIG. 1. DLTS spectra of sample *A* (a) and sample *B* (b) after annealing for 15 min at temperatures ⩾200 °C.

The effect of hydrogenation on the annealing behavior of V_2 is clearly seen at the annealing temperatures >200 °C (Fig. 1). The amplitudes of the observed major peaks as a function of annealing temperature are presented in Fig. 2. In the nonhydrogenated sample [Fig. 1(a)], heat treatments for 15 min at 250 and 275 °C lead to the transformation of V_2 to V_2O almost without any loss in the peak intensity. The transformation is completed after 15 min at 300 °C. The V_2O

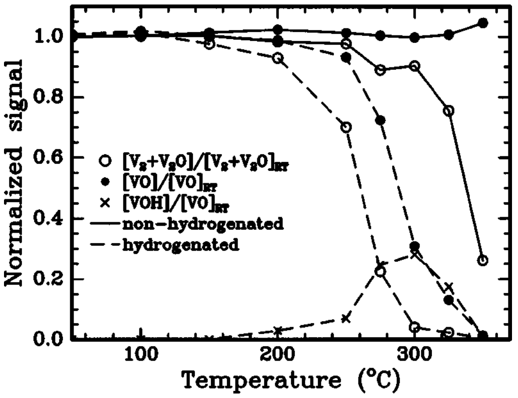

FIG. 2. Normalized amplitudes of the major DLTS peaks as a function of annealing temperature. The concentration $[V_2+V_2O]$ is deduced from the amplitudes of the $V_2(=/-)$ and $V_2O(=/-)$ peaks.

peaks start to anneal out at 325 °C and are considerably reduced after 15 min at 350 °C (Fig. 2). In contrast, the hydrogenated sample [Fig. 1(b)] reveals that the V_2 peaks already start to disappear at 250 °C, and a significant loss of the amplitude occurs. After a heat treatment at 275 °C approximately 80% of the initial amount of V_2 is annealed out. It should be noted that a shift in the peak maxima is observed after the heat treatment at 275 °C [Fig. 1(b)], indicating that some limited transformation of V_2 to V_2O also takes place in the hydrogenated sample. After heat treatment at 300 °C, no signals from V_2 and V_2O can be observed in the spectra for sample *B*.

A minor peak at ~160 K emerges in sample *A* after heat treatments at 275 and 300 °C [Fig. 1(a)]. The origin of this peak is not readily identified. It can be seen, however, that the growth in the amplitude of this peak does not correspond quantitatively to the change in the amplitudes of the major peaks. In the following, we will focus only on the V_2, V_2O, and VO peaks.

An evidence of the considerable hydrogen concentration in the hydrogenated sample *B* is obtained from the annealing behavior of VO. As revealed by Figs. 1(a) and 2, the VO peak is stable up to $\geqslant$350 °C in the nonhydrogenated sample, while in the hydrogenated sample VO anneals at 275–300 °C with the formation of VOH [Figs. 1(b) and 2]. The transformation of VO to VOH via interaction with atomic hydrogen, $VO+H\rightarrow VOH$, has been observed in a number of experiments.[6,12–14] The annealing of VOH is due to capture of a second hydrogen atom with formation of VOH_2, which is electrically inactive.

The annealing behavior of V_2 in the hydrogenated sample *B* [Fig. 1(b)], where the disappearance of V_2 occurs before the formation of V_2O, demonstrates that the interaction of V_2 with hydrogen takes place at a higher rate than that with oxygen. Thus, one can conclude that a dominant mechanism of impurity-assisted annealing of V_2 invokes hydrogen. This conclusion, however, can be argued since no significant formation of the divacancy-hydrogen complex (V_2H) is observed. V_2H is known to have one deep acceptor level with the activation energy 0.43 eV, almost identical to that of $V_2(-/0)$,[12,15] so it cannot be readily resolved in DLTS spectra. The formation of V_2H during V_2 annealing would result in an asymmetrical loss in the amplitude of the peaks labeled $V_2(=/-)$ and $V_2(-/0)$, where the amplitude of the peak labeled as $V_2(=/-)$ would decrease at a faster rate than that labeled as $V_2(-/0)$. This has not been observed in the present study. On the contrary, Fig. 3 shows that the amplitudes of the $V_2(=/-)$ and $V_2(-/0)$ peaks decrease simultaneously with a close one-to-one ratio. This rules out the interaction $V_2+H\rightarrow V_2H$ as a dominant mechanism.

It is well established that hydrogen in Si is either trapped in complexes with other impurities stable up to 300 °C (Ref. 16 and references therein) or in a form of dimers.[17–19] Two types of hydrogen dimers have been suggested: (i) molecular hydrogen (H_2) (Refs. 17 and 18) and (ii) the so-called H_2^* complex.[19] It has been found that a significant fraction of hydrogen in moderately doped Cz-Si is in the form of H_2 and can be observed as isolated interstitial molecules[17,18] or as O-H_2 complexes.[20] At temperatures above 200 °C, a considerable fraction of H_2 is expected to be in the form of isolated interstitial molecules since the binding energy of the O-H_2 complex is relatively low, ~0.3 eV,[21] and the activation energy for migration of H_2 is estimated to be ~0.8 eV.[21]

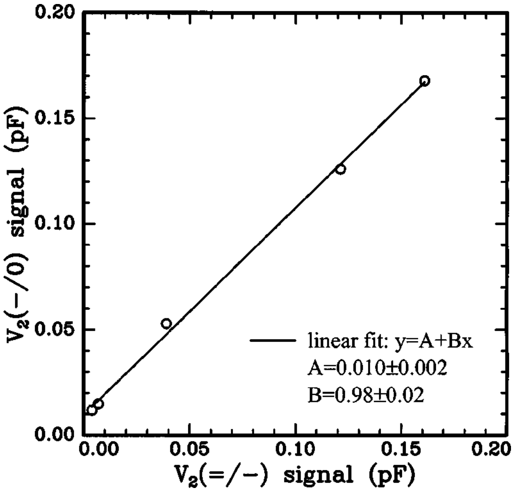

FIG. 3. The amplitude of the peak labeled $V_2(-/0)$ vs that of the peak labeled $V_2(=/-)$ in sample *B* during annealing. The solid line represents a linear fit to the experimental data.

The second form of hydrogen dimer, H_2^*, has been observed in Si irradiated with protons and deuterons at room temperature.[19] The transformation of H_2 to H_2^* at room temperature has been explained in terms of the interaction of H_2 with monovacancies (V) and interstitials (I) during irradiation.[22] It has been theoretically shown that it is energetically favorable for H_2 to break the H-H bond and form the Si-H bonds when H_2 meets V or I. Thus, interaction of H_2 with V or I results in formation of {V,H,H} or {I,H,H} complexes that is followed by annihilation with I or V, respectively, and formation of H_2^*.[22]

Based on the above considerations, it is possible to assume that (1) the isolated interstitial H_2 is the dominant form of mobile hydrogen at 200–300 °C, and (2) interaction of H_2 with V_2, which has two dangling bonds,[4] can result in the break up of the H-H bond and formation of Si-H bonds, similar to the interaction of H_2 with V.[22] In this case, the V_2H_2 complex can be formed directly via the interaction $V_2+H_2\rightarrow V_2H_2$, without formation of the intermediate V_2H complex, at 200–300 °C. It is not yet experimentally established whether V_2H_2 is electrically active or not. It is expected from calculations that V_2H_2 has a relatively shallow acceptor level (within 0.2 eV below the conduction band).[23] However, to the best of our knowledge, no observation of an electronic level identified as V_2H_2 has been reported.

The annealing results in Figs. 1(b) and 2 show that at least a fraction of the VO centers anneals via formation of VOH. It can be speculated that the interaction of VO with H_2 is less energetically favorable than that of V_2. Indeed, unlike V_2, VO does not have dangling Si bonds and the electrical activity of VO arises from the reconstructed Si-Si bond.[24] Thus, in order to interact with H_2, the reconstructed Si-Si bond must be broken first. This requires energy and is likely to decrease the probability of the interaction between VO and H_2. The fact that VO anneals out at higher temperatures as compared to V_2 (Fig. 2) supports this consideration. At higher temperatures, the concentration of free atomic hydrogen increases due to release of trapped H from complexes and, possibly, dissociation of H_2, and the interactions $VO+H \rightarrow VOH$ and $VOH+H \rightarrow VOH_2$ are promoted.[6] Further, simultaneous annealing of VO via the interaction $VO+H_2 \rightarrow VOH_2$ may also occur at higher temperatures.

The annealing behavior of VO in the present study differs considerably from that reported by Markevich *et al.*,[25] where the annealing of VO has been observed in a temperature range from 100 to 300 °C and attributed to the interaction $VO+H_2 \rightarrow VOH_2$. Several explanations for this discrepancy with the present results can be given. First, the hydrogenation in Ref. 25 has been performed in a H_2 atmosphere at 1200 °C, which can result in a different hydrogen content, as compared to the low-temperature plasma hydrogenation in the present study. Second, the unusually wide temperature range (100–300 °C) for the annealing of VO suggests multiple mechanisms of the VO interaction with hydrogen and/or multiple sources of free mobile hydrogen species. Third, it can be argued that at least a fraction of VO anneals via interaction with atomic H and formation of VOH. Indeed, one can observe a peak at 872 cm^{-1} in the infrared absorption spectra in Ref. 25 which is close to a previously reported absorption band at 870 cm^{-1} identified as VOH.[26] Hence, a detailed kinetic study invoking the infrared bands assigned to VO, VOH, VOH_2, and OH_2 would be highly desirable to reveal this apparent discrepancy for the VO annealing.

In conclusion, we have performed comparative DLTS studies of high-purity oxygenated Si with and without intentionally introduced hydrogen. It is shown that the nonhydrogenated samples demonstrate a transition of V_2 to V_2O with a close one-to-one correlation, while the hydrogenated samples exhibit annealing of V_2 without a corresponding formation of V_2O or other electrically active centers. A mechanism for hydrogen assisted annealing of V_2 is proposed, invoking interaction of V_2 with mobile H_2 molecules that results in the direct formation of V_2H_2.

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