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Positron annihilation study of divacancies in silicon illuminated by monochromatic light

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The charge of divacancies in undoped float-zone silicon has been investigated as a function of photon energies between 0.2 and 1.2 eV by means of positron lifetime spectroscopy. For photon energies between 0.25 and 0.65 eV and above 0.75 eV, negatively charged vacancies were formed, whereas in the 0.65 to 0.75 eV range there was no effect from illumination. The results are explainable on the basis of Watkins and Corbett's model of divacancy [Phys. Rev. **138**, A543 (1965)]. Evidence was found that the radioactive positron source significantly reduces the stability of the photon-induced population of negatively charged divacancies, an effect which is invoked to explain the apparently anomalous results reported by Kawasuso and Okada [Jpn. J. Appl. Phys., Part 1 **36**, 605 (1997)]. [S0163-1829(99)05127-9]

I. INTRODUCTION

Divacancy in silicon has been investigated by infrared absorption,[1–4] electron paramagnetic resonance (EPR),[5] and electron nuclear double resonance (ENDOR),[6,7] photoconductivity,[1,8–10] and deep-level transient spectroscopy (DLTS),[11] and a theoretical framework has been provided for by the model of Watkins and Corbett.[5] From all of these investigations three electronic levels are found in the band gap, bracketing the four V_2^+, V_2^0, V_2^-, and V_2^{2-} charge states of the divacancy: further states are situated in the valence or conduction bands.

The $+/0$ level is consistently determined to be 0.2–0.3 eV above the valence-band edge. For the $0/-$level, a larger scatter of 0.54–0.40 eV below the conduction-band edge is found as is the case for the $-/--$ level (at 0.2–0.4 eV below the conduction-band edge). Considering the diverse experimental conditions (temperature, irradiation type, dose, and sample types) these level determinations are remarkably consistent, albeit details in interpretations sometimes lead to seemingly contradictory conclusions.

The positron experiments described in this work concern changes in charge states of divacancies resulting from illumination and are hence linked to photoconductivity measurements, but because positron measurements are spectroscopic in that they identify the vacancy type which changes charge, in contrast to photoconductivity, they also relate to EPR/ENDOR data. In a recent work[12] we have established that divacancies are the main trap for positrons in samples similar to those investigated in this work.

Positron experiments combined with illumination are scarcely reported in the literature. An early investigation on GaAs demonstrated that illumination has an influence[13] and, more recently, the EL2 defect in GaAs (Ref. 14) and the arsenic vacancy,[15] were investigated. In a work closely related to the present one, Kauppinen *et al.*[16] investigated divacancies in Si for photon energies above 0.7 eV.

II. EXPERIMENT

Electron-irradiated samples investigated in this work were similar to those used earlier,[12] i.e., cut from the same block of undoped float-zone Si material. The electron dose was $1.2\times10^{18}\,e^-/\mathrm{cm}^2$ at 10 MeV and the temperature of the samples during the irradiation was 8 °C. Each lifetime spectrum was accumulated to a fairly low amount of counts, 2×10^6 over a time interval of 2×10^4 s and repeated three times. This procedure was chosen as a compromise between the ability to detect possible time developments when applying or removing light and being able to acquire a bare minimum of counts necessary for the numerical analysis of the spectra.[17]

The positron source had a strength of 14 μCi (0.5 MBq) and was deposited on a 0.8-μm-thick Al foil. The source (with a diameter of 0.8 mm) was placed 2 mm from the edges of the samples onto which the light was shone, i.e., the samples were illuminated ''sideways.'' The illumination was done using a 100-W halogen lamp, an Oriel 1/8-m monochromator, and a concave Al mirror to focus the light onto a $2\times8\,\mathrm{mm}^2$ spot size on the samples. To cover the photon energy range of 0.2 to 1.2 eV three different monochromator gratings were used, each operated within their primary wavelength range (0.6–1.5 μm, 1.33–3.0 μm, and 2.67–6.0 μm) and with bandwidths of 16, 32, and 64 nm, respectively. Although the photon flux was not monitored in these experiments, subsequent flux measurements were done using a thermopile detector. For each grating the intensity decreases, according to standard grating data, by a factor of 2 on either side of the blazing wavelength for the grating. For wavelengths larger than ~5 μm the intensity is further reduced due to the quartz envelope of the lamp as well as due to the quartz window in the cryostat. At 6 μm the spectral photon flux is about $1\times10^{14}\,\mathrm{cm}^{-2}\,\mathrm{s}^{-1}\,\mathrm{nm}^{-1}$. The maximum spectral photon flux entering into the samples is calculated to be about $1\times10^{15}\,\mathrm{cm}^{-2}\,\mathrm{s}^{-1}\,\mathrm{nm}^{-1}$ for each of the gratings after taking into account the reflectivity of silicon.

The light was filtered by a Si wafer before entering the samples to remove higher orders from the monochromator. An InAs filter was also used in the 0.2 to 0.35 eV photon range since here the Si filter does not cut out higher orders; there was no difference between the results when using the two filters. In changing from one experimental condition to another (photon energy, temperature, or light intensity) the samples were kept in darkness for 2 h before commencement

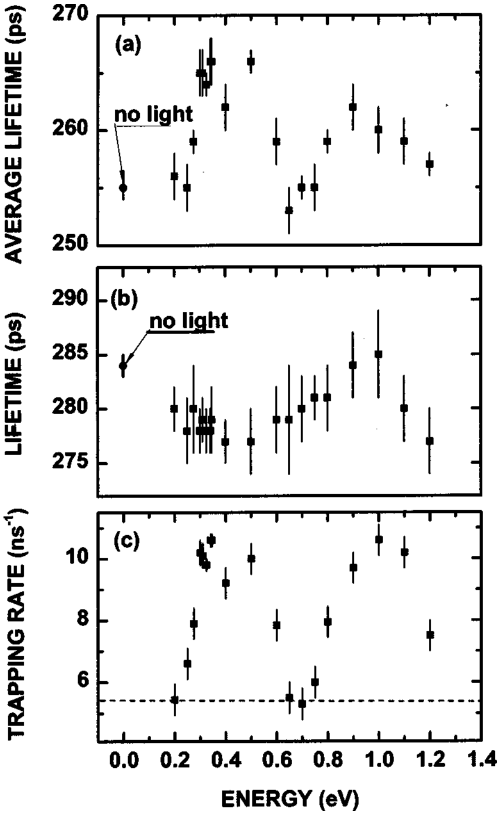

FIG. 1. Average positron lifetime (a), positron lifetime for divacancies (b), and associated trapping rate (c) as a function of photon energy at 20 K. The dashed line at 5.5 ns^{-1} corresponds to the trapping rate for dark condition.

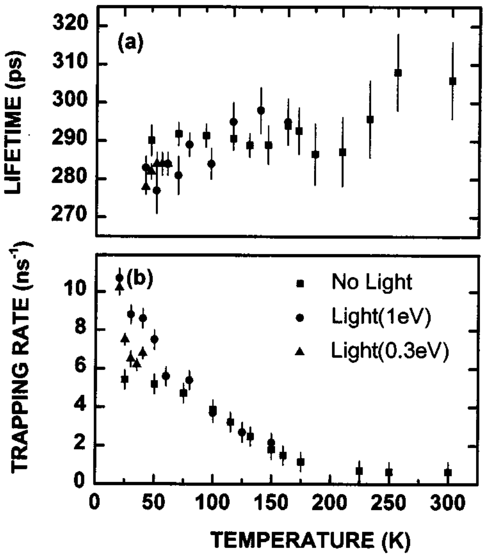

FIG. 2. Temperature dependence of positron lifetime for divacancies (a) and trapping rate (b) at indicated photon energies. The data for the dark condition are from Ref. 12. using identical samples.

of measurements in the new condition (except in the case of investigating time dependencies), ensuring that the samples start out from a common dark condition as will be substantiated in the next section.

Analyses of lifetime spectra yield data for lifetimes and associated intensities. Based on these the average lifetime $\tau_{avg}=I_1\tau_1+I_2\tau_2$ is calculated and, via the trapping model,[18] the trapping rate for divacancies. This rate, κ, was calculated in two different ways, either as $\kappa=1/\tau_1-\tau_B$ or as $\kappa=(1/\tau_B-1/\tau_2)I_2/(1-I_2)$, where τ_B is the bulk lifetime (217 ps).[12] Within error bars both methods gave the same values as based on unconstrained analyses of the lifetime spectra thus supporting the applicability of the trapping model.

The trapping rate is proportional to the divacancy concentration according to

$$\kappa=\mu[V_2]. \tag{1}$$

The absolute specific trapping rate, μ, depends on the charge of the divacancy. For neutral divacancies, $\mu(=\mu^0)$ is independent of temperature while for negatively charged divacancies, μ^- increases with decreasing temperature.[19,20] At low temperature μ^- is much larger than μ^0 thus strongly enhancing the positron response from V_2^- relative to that of V_2^0.

III. RESULTS

In Fig. 1(a) we show the average lifetime. In 1(b) we show the positron lifetime for divacancies and in 1(c) we show the trapping rate as a function of photon energy at 20 K. The broken line at the trapping rate of 5.5 ns^{-1} signifies the value in darkness which is identical to that reported earlier.[12] In unirradiated Fz-Si no light-induced effects were found. The calculated bulk lifetime was constant (at 218 ± 3 ps) between 20 and 300 K.

The trapping rate increases rapidly above 0.2 eV and there is an indication for a valley at 0.4 eV. Close to 0.7 eV there is no effect from the illumination as also found by Kauppinen *et al.*[16] in float-zone Si, and the subsequent increase in trapping rate by a factor of 2 was also found by Kauppinen *et al.*[16] These changes in trapping rates are reversible as far as light-on, light-off is concerned, and no ''memory'' effect could be detected in the sense that the effect arising at one photon energy was independent of former photon energies applied to the sample.

The light intensity was sufficient to increase the trapping rate well within the time necessary for a positron measurement (2×10^4 s) and relaxation to a dark condition (by turning off the light) also took place well within 2×10^4 s (an upper limit is $\sim6\times10^3$ s); Kauppinen *et al.*[16] made the same observations. In these particular experiments measurements started immediately after turning off the light since the purpose was to look for relaxation toward the dark condition. Although this explains why no memory effect was observed, due to the normally employed 2-h waiting period in darkness, the rapid relaxation is surprising considering that Cheng, Corelli, Corbett, and Watkins[2] and Svensson, Svensson, and Monemar[4] report relaxation times of several hours in their EPR and optical experiments. As described in Sec. IV we attribute the rapid relaxation to the positrons since, with an average kinetic energy of 300 keV, they are capable of producing many electron-hole pairs.

The temperature dependence of the trapping rate was investigated at two photon energies, 0.3 and 1.0 eV. In Fig. 2

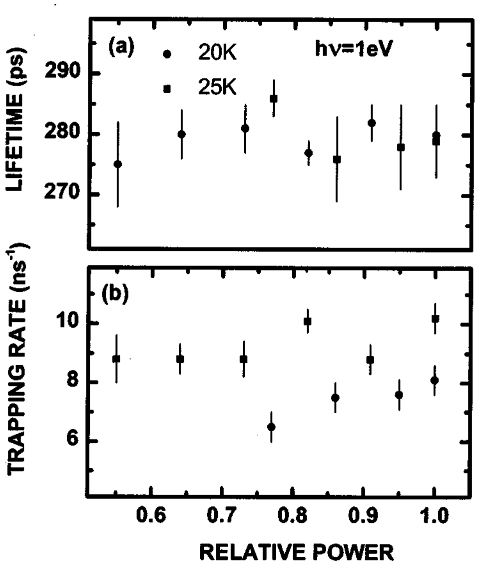

FIG. 3. Dependence of lifetime (a) and trapping rate (b) on the relative power supplied to the halogen lamp. The light intensity is estimated to change by a factor of 5. Dark condition is indicated by the dashed line in panel (b).

we show the data, together with those for samples in darkness (from Ref. 12). At 0.3 eV the effect from the photons is observable below ≃35 K whereas for 1.0 eV it persists to ≃60 K which agrees well with the work of Kauppinen *et al.*[16] using 1-eV photons.

We also investigated the influence from the light intensity (at 1.0 eV), albeit in a rather cursory manner by reducing the voltage on the halogen lamp (which changes the spectral distribution) and at half the nominal power the intensity of the light has decreased by a factor of 5. Figure 3 shows that the trapping rate increases little with power at 20 K, indicating near saturation, but at 25 K a more pronounced effect is found.

During the changes in the trapping rate as a function of either photon energy, temperature, or illumination intensity there was no marked change in the positron lifetime, which indicates that the changes in the trapping rates are caused by the same structural defect, i.e., the divacancy.

IV. DISCUSSION

Since the photon flux was not maintained at a constant level in the present experiments the detailed variations in the data for the trapping rate in Fig. 1(b) could be influenced by flux variations. However, the data in Fig. 3 show that a decrease in flux by a factor of 5 has little effect on the trapping rate, as also found by Kauppinen *et al.*[16] Details, such as if there really is a valley at 0.4 eV, must await further investigations using constant photon flux, but the main features are surely not influenced by flux variations as is evident by the close similarity of our data above 0.7 eV to those of Kauppinen *et al.*[16] who used a constant flux.

To explain the results we start with the basic notion that electrons must be transferred to divacancies in order to increase their trapping rate. These electrons can under illumination originate from different sources: (i) from the valence band and (ii) from other defects giving electrons to the conduction band from where they may subsequently be trapped by divacancies. If the latter were the case then to explain the rapid increase in trapping rate above the photon energy at 0.25 eV would require an electronic level 0.25 eV below the conduction band from which the electrons are excited. We are not aware of any such level and mention, in particular, that the oxygen-vacancy pair (a center, which could be formed during irradiation with residual oxygen in float-zone Si) is not a likely source because its electronic level is situated at 0.17 eV below the conduction band.[21]

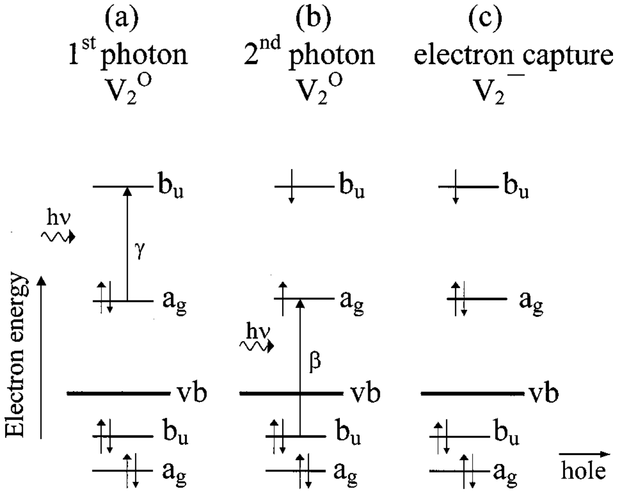

FIG. 4. Proposed mechanism for the two-photon-induced $V_2^0 \rightarrow V_2^-$ change in charge at the photon energy close to 0.32 eV. In (a) the neutral vacancy is excited by the γ transition, stable long enough that a second photon (b) can cause the β transition. An electron in the valence band (VB) is subsequently trapped at the half-full b_u state and a hole is emitted (c).

Instead we suggest that divacancies can be turned negatively charged by photoexcitation of electrons in the valence band: It is an essential part of this interpretation that a mixture of V_2^0 and V_2^- is present in the dark condition at 20 K, although V_2^- is the defect which contributes overwhelmingly to the trapping rate (due to their negative charge), because without V_2^0 it would not seem possible to explain the rapid increase in trapping rate slightly above 0.2 eV. Figure 4 reproduces the Watkins and Corbett electronic level scheme for divacancy.[5] Two electron-filled levels are situated in the valence band, and electrons, one in the case of V_2^+, two in the case of V_2^0, can occupy the band gap state a_g. To explain the 0.3-eV photon-induced increase in charge we invoke a two-photon process, in which the first involves excitation of V_2^0 from the filled a_g state in the band gap to the empty b_u state by means of the γ transition [Fig. 4(a)]. The emptying of one electron from the a_g state then makes possible the β transition [Fig. 4(b)] by a second photon. Although these two processes do not change the charge state of V_2^0, subsequent trapping of an electron in the valence band at the partially emptied b_u state does, converting V_2^0 into V_2^- [Fig. 4(c)], and a hole is consequently created. If only V_2^- were present, charging (to produce V_2^{2-}) would have required a photon energy of at least 0.7 eV, for which reason V_2^0 was invoked to explain the 0.32-eV photon-induced increase in the trapping rate.

Three conditions must be met (apart from the necessity for V_2^0) for the above process. (i) The photon energy of 0.32 eV must be capable of exciting both the γ and β transitions. (ii) The lifetime of the excited V_2^0 state created by the first photon must be long compared to the time necessary for the second photon absorption to take place, and to this requirement we ascribe the low temperature (<35 K) necessary for observation. (iii) There must be traps for the holes produced due to the second photon (this does not follow directly from the positron experiments but does from the thermal stability of V_2^- observed in EPR (Ref. 2) and optical experiments[4]). These traps, which are also necessary for the higher photon energies, must be deep enough to prevent hole migration up to $\simeq 60$ K. The hole traps are likely caused by valence band-edge fluctuations giving rise to the well-known irradiation-produced featureless near-band-gap absorption[1,8] (which was also observed in our sample).

The indication for a valley at 0.4 eV in the trapping rate is somewhat dubious since it could be influenced by photon flux variations. However, because the γ transition is expected to be energetically well defined a peaked structure at 0.32 eV would be expected, so the continued high trapping rate for higher photon energies suggests another mechanism for charging V_2^0, namely a one-photon excitation directly from the valence band into the empty b_u level in the band gap. Kalma and Corelli's measurements[8] support this by virtue of a step in photoconductivity at 0.42 eV (at 78 K). This step was clearly observable for a relatively small electron dose ($5\times10^{16}\,e^-/\mathrm{cm}^2$), but severely broadened at a dose of $1\times10^{18}\,e^-/\mathrm{cm}^2$, close to that employed in this work: This broadening we ascribe again to fluctuations of the valence band relative to the b_u level.

The subsequent decrease in trapping rate to the dark level (at 0.65 eV) shows that electrons are removed from V_2^- and this we suggest is due to photoexcitation of electrons into the conduction band converting V_2^- into V_2^0. Kalma and Corelli's measurements[8] support this interpretation by virtue of the observation of a photoconductivity step at 0.54 eV, which too is broadened at high electron dose. Thus the broad ''peak'' centered at 0.5 eV can be explained as a result of competition between photoexcitation of electrons in the valence band to V_2^0 and photoexcitation of electrons in V_2^- into the conduction band reverting V_2^- back to V_2^0. This implies that the $0/-$ level is situated close to the midgap position.

Between 0.65 and 0.75 eV photons cause no increase in the trapping rate relative to the dark condition. It is in this range the so-called 1.8-μm optical absorption band is situated (0.72 eV at 20 K) which, according to Fan and Ramdas,[1] does not result in photoconductivity, and was hence suggested[1,2] to arise from population of an excited state of the divacancy. The positron results support this interpretation since excitation does not change the charge state.

For photon energies higher than 0.75 eV the increase in trapping rate (peaking at 1.0 eV) can have at least two possible causes. One is due to direct excitation of valence electrons to the $-/--$ level of V_2, but smeared due to the high electron dose. The other (indirect) is due to excitation of valence electrons to the conduction band with subsequent trapping at V_2^0. Kauppinen *et al.*[16] concluded that V_2^{2-} is formed at photon energies larger than 0.75 eV, and although our data could be explained likewise, we do point out that V_2^- formation is also possible in view of the experiments of Carton-Merlet *et al.*,[3] where it was found that optical absorption due to V^- could be induced by photon energies either below or above 0.7 eV.

It was originally argued that in our samples a mixture of V_2^0 and V_2^- was present in darkness, and we estimate that about 1/2 of the divacancies are neutral at 20 K based on the observations that the trapping rate doubles relative to the dark condition and that this effect is in near saturation (at 20 K), according to Fig. 3.

The observation that positrons reduce the stability of the light-induced concentration of V_2^- (in EPR and IR experiments they were stable for many hours after the light was turned off, whereas they were not in the positron experiments) indicates that injection of positrons affects the population of V_2 charge states, and this leads us to speculate on the cause for the ''anomalous'' temperature dependence of the trapping rate observed by Kawasuso and Okada,[22] who found that the trapping rate decreased strongly with increasing temperature (from 10 K), an effect normally ascribed to negatively charged defects (divacancies in this case). However, according to their EPR and infrared data, there was no evidence for V_2^- (although such could be produced by illumination), so they concluded that V_2^0 also has a strongly temperature-dependent trapping rate. Instead we offer the explanation that positrons, which enter into the samples with an average kinetic energy of 300 keV, cause electron-hole pair generation which, at low temperatures, converts some V_2^0 into V_2^- as in the case of band-gap light.[22] These V_2^- are then responsible for the temperature dependence of the trapping rate in darkness, but would not, of course, show up in EPR or in optical measurements. Although charging of vacancies in semiconductors by positrons has not been reported to the authors' knowledge, there is clear evidence that this happens in alkali-halides.[23]

To estimate the numerical feasibility of this effect, a positron source of 14 μCi would create about 10^{10} electron-hole pairs/s in the volume of $10^{-4}\,\mathrm{cm}^3$ probed by the positrons, i.e., about 10^{14} electron-hole pairs/cm^3/s. Thus in only 100 s enough would be created to be comparable to the divacancy concentration of $\sim10^{16}/\mathrm{cm}^3$ produced by the electron irradiation (based on an introduction rate[24] of 0.01 cm^{-1}). This charging time is clearly an underestimate, but since a positron experiment in our case lasts 2×10^4 s, the time can be extended by a factor of ≈ 50 without leading to a measurable effect in a lifetime spectrum.

One can only expect that positron-induced charging will depend on doping concentration and other impurities as well as on temperature; for example, in a medium to heavily doped *p*-type material the hole concentration would likely prevent charging as indeed is observed in $10^{17}/\mathrm{cm}^3$ *B*-doped silicon[25] as well as in doped GaAs.[13] The above considerations raise the possibility that in some cases positron annihilation experiments may modify the very defect inventory under investigation, and such cannot be excluded in the present work, but would not alter the phenomenae arising from the illumination.

V. CONCLUSION

Positron annihilation detects charge states of divacancies in silicon as modified by monochromatic light. Transfer of an electron to V_2^0 can be accomplished via a two-photon absorption process close to 0.3 eV while a one-photon mediated electron transfer occurs between 0.4 and 0.6 eV. Trapping of holes thus produced is suggested to be accomplished by irradiation-produced fluctuations in the valence bandedge. Photoexcitation at 0.65–0.75 eV causes no deviation from the dark situation confirming that at these photon energies the optical absorption band at 0.72 eV does not involve a change in charge state of the divacancies. At photon energies above 0.75 eV, V^- as well as V^{2-} can be formed.

This work raises the possibility—or concern—that positrons by means of production of carriers are capable of changing the charge state of V_2^0 in silicon at low temperatures, just as in the case for band-gap light, and we see no reason why such should be restricted only to divacancy in silicon.

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