

## Charge redistribution among defects in heavily damaged silicon

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 (Received 9 February 1998)

We have studied trapping kinetics of defects during carrier capture in heavily damaged silicon, where damage was induced by MeV heavy ions at doses near but below the amorphization threshold. Using spectroscopic junction transient measurements, we provide unambiguous evidence of charge redistribution between defects. These results imply that changes in the *occupancy* of gap states are responsible for the deepening of emission energies with filling time, as is commonly observed in transient experiments in disordered silicon. This is in contrast to its usual explanation in terms of deepening of energy states due to hierarchical defect relaxation. [S0163-1829(98)01323-X]

The presence of continuously distributed defect energy states in disordered silicon has been central to many controversies, specifically in relation to the determination of density of states (DOS), effective correlation energies, and mechanisms of charge relaxation. The trapping kinetics of defects have been studied through a rich variety of experiments, and has led to a long-standing debate on whether defect relaxation needs to be invoked in the interpretation of the results. The controversy has been essentially between whether DOS itself changes due to lattice relaxation, defect formation, etc., or DOS is fixed and its changed occupancy with time is responsible for the observed dynamics in these experiments. A study of the capture of carriers at gap states in amorphous silicon (*a*-Si) using junction capacitance led Cohen, Leen, and Rasmussen<sup>1</sup> to propose a novel hierarchical defect relaxation mechanism in which polarization around negatively charged defects causes relaxation and drives the average emission energy deeper into the gap. However, an alternative explanation of their transient data was proposed by Farmer and Su,<sup>2</sup> who invoked charge redistribution from shallower to deeper levels through multiple trapping at gap states distributed exponentially with energy. In either case, comparison with experimental transients required convolution with a broad density of states, and hence distinction between models remains equivocal as evidenced in a series of contributions on the issue.<sup>3-7</sup>

The question that motivates us is whether it is possible to resolve controversies such as these, which would involve distinguishing between defect relaxation and multiple trapping effects by studying defect phenomena in the presence of disorder prior to complete amorphization. In general terms, the relation between disorder and gap states would be more revealing when studied in a regime wherein there are a large number of defects that retain their identity and yet are sensitive to disorder. Such an opportunity is provided by MeV heavy ion implantation in silicon due to its ability to create a controlled degree of damage. In addition, the study of defects in heavily damaged silicon has recently attracted considerable attention<sup>8-10</sup> due to its technological significance.

In this paper, we seek to study defect charge relaxation in heavily damaged silicon with a controlled degree of disorder using spectroscopic junction capacitance transient measurements. The damaged layer produced by heavy MeV im-

planted ions is embedded within the depletion layer of a Schottky diode. Time analyzed transient spectroscopy (TATS),<sup>11</sup> which involves DLTS-like (deep level transient spectroscopy) analysis of isothermal transients in the time domain, has been used to show an unambiguous signature of charge redistribution among discrete trap levels.

Phosphorus-doped  $n^+/n$  silicon wafers with resistivity 2–5  $\Omega$  cm in the epitaxial layer with vacuum annealed back Ohmic contacts were irradiated from the front side at room temperature with 1.45 MeV Ar<sup>+</sup> ions using a 2 MeV Van de Graaff accelerator. Ion doses of  $5 \times 10^{13}$  cm<sup>-2</sup> and  $1 \times 10^{14}$  cm<sup>-2</sup> were used to create damage just below the amorphization threshold.<sup>12</sup> Schottky contacts were made with evaporated gold dots. The as-implanted samples did not receive any other high-temperature annealing except for heating at 70 °C for 30 min for curing the contact epoxy. Capacitance measurements were done using a Boonton capacitance meter (model 72B) operated at 1 MHz.

Figure 1 shows a typical DLTS spectrum of a sample implanted with  $5 \times 10^{13}$  Ar<sup>+</sup> ions cm<sup>-2</sup>. The peak marked P1 is generally attributed to a divacancy and/or a phosphorus-vacancy complex,<sup>13</sup> and has been observed by a large number of authors working with ion implanted or electron-proton irradiated *n*-type silicon. The defect corresponding to peak P2 occurs in large concentration in our samples irradiated at high fluence. Previous studies do not report this peak, perhaps because they were carried out with

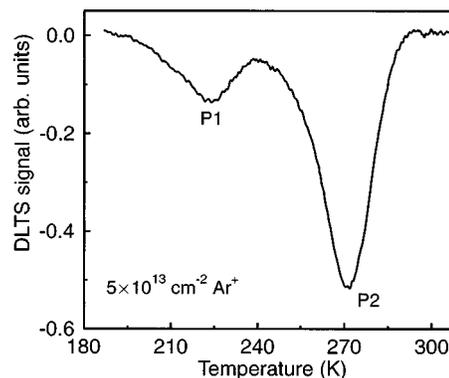


FIG. 1. A typical DLTS spectrum for Ar<sup>+</sup>-irradiated *n*-Si plotted for rate window:  $e_n = 63$  s<sup>-1</sup>.

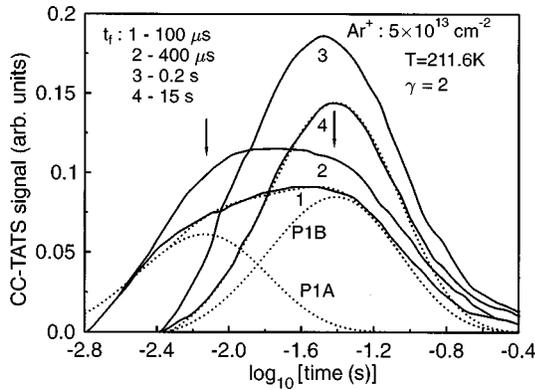


FIG. 2. Second-order TATS spectra of peak  $P1$  for filling times varying from  $100 \mu\text{s}$  to  $15 \text{ s}$ . Arrows indicate the apparent peak position for two different centers  $P1A$ ,  $P1B$ . For curve 1, contributions from the two constituent peaks ( $P1A$ ,  $P1B$ ) and the result obtained by fitting are shown by dotted lines. Curve 4 could be fitted with one peak ( $P1B$ ) only as shown. Gaussian broadening with FWHM of  $\approx 10 \text{ meV}$  in activation energy was assumed for fitting in each case.

low fluences of heavy ions<sup>13</sup> or after post-implantation annealing.

DLTS, being a temperature scanning technique, has severe limitations in the study of detailed line shape in terms of broadening and multiplicity. Further, it is unsuitable for monitoring changes in degree of filling of multiple levels at any particular temperature of interest. Hence, in order to unravel any possible coupling of kinetics of capture and to achieve sufficient resolvability, we resorted to isothermal transient spectroscopy. TATS (Ref. 11) is such a spectroscopy based on a sweeping rate window in the time domain, which is in contrast to DLTS where the rate window is kept fixed and the temperature is varied. The first-order ( $S_1$ ) and second-order ( $S_2$ ) TATS signals are

$$S_1(t) = V(t) - V[(1 + \gamma)t] \quad (1)$$

and

$$S_2(t) = V(t) - 1.5V[(1 + \gamma)t] + 0.5V[(1 + \gamma)^2t], \quad (2)$$

where  $V(t)$  is the constant capacitance (CC) voltage transient and  $\gamma$  is a selectable experimental constant. We have shown elsewhere<sup>11</sup> that various orders of TATS can be viewed as difference operators corresponding to differentiation of the transient signal with respect to  $\ln(t)$ . TATS has been found to be extremely useful in spectroscopic line-shape analysis, which often offers valuable insights into the physics of defects. The choice of order of spectroscopy is guided by the required compromise between resolvability and signal-to-noise ratio. Since the peak  $P1$  has been associated with two different defects in the literature,<sup>13</sup> we choose second-order TATS for its analysis in order to be able to resolve possible multiplicity in line shape.

Figure 2 shows second-order CC-TATS spectra of the defect corresponding to peak  $P1$  for several filling times. The spectra corresponding to large filling times (curve 4) are fitted to a single emitting center ( $P1B$ ) assuming a small Gaussian broadening with FWHM (full width at half maximum) of  $10 \text{ meV}$ . For lower filling times the reconstruction

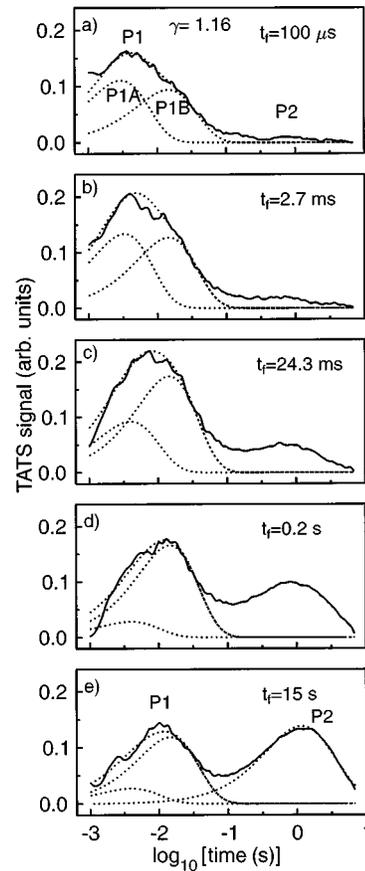


FIG. 3. First-order TATS spectra at  $217.6 \text{ K}$  for different filling times ( $t_f$ ) showing progressive changes in occupancy for high dose ( $1 \times 10^{14} \text{ cm}^{-2}$ ) implanted sample. Peak  $P1$  is fitted (dotted line) to two different centers  $P1A$  and  $P1B$ , and peak  $P2$  is fitted to a Gaussian broadened peak with a FWHM of  $25 \text{ meV}$  and the fitting is shown by a separate dotted line in frame (e).

of line shape requires contribution from another fast emitting center ( $P1A$ ) with similar broadening, as shown by fitting to curve 1. The variation in intensities corresponding to these distinct emitting centers shows that changes in occupancy with filling time are nonmonotonic. An unambiguous demonstration of the two-peak nature of this spectrum is clearly central to the understanding of carrier capture kinetics.

To quantitatively evaluate occupancy changes of all three peaks  $P1A$ ,  $P1B$ , and  $P2$ , we used first-order TATS spectra for filling times varying over five orders in magnitude. A typical set of such spectra is shown in Fig. 3 [frames (a) to (e)] for progressively increasing filling times. To explain the spectra, the relative concentration of the constituents has been evaluated by fitting contributions from three different defects. The emission time constants of  $P1B$  and  $P2$  have been obtained from their respective peak positions in the spectra in the long pulse limit. The emission time constant of  $P1A$  is then estimated from experimental spectra. All time constants ( $\tau_e$ ) are kept fixed for varying filling times, while the relative concentrations of the peaks are treated as free parameters in the fitting. In the frame (e) of Fig. 3, a fitting to the peak  $P2$  is also shown. This was done using a Gaussian with FWHM of  $25 \text{ meV}$  in energy. However, the FWHM needed for the same peak for the lower dose (5

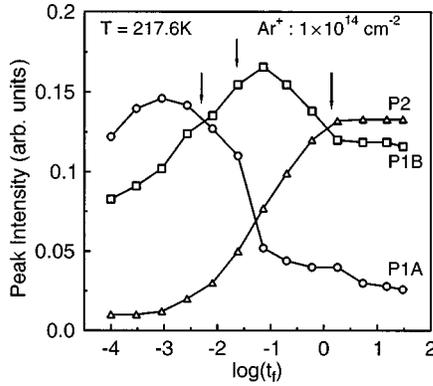


FIG. 4. Relative intensity of individual peak as a function of filling time for  $\text{Ar}^+$  ion dose of  $1 \times 10^{14} \text{ cm}^{-2}$ . Vertical arrows indicate the measured emission time constants ( $P1A$ , 5 ms;  $P1B$ , 25 ms;  $P2$ , 1.43 s) for the corresponding centers at 217.6 K.

$\times 10^{13} \text{ cm}^{-2}$ ) sample was 6 meV. Peaks  $P1A$  and  $P1B$  show similar small broadening only in the high dose sample.

The peak intensities obtained from the analysis have been plotted as a function of the logarithm of filling time in Fig. 4. Peak  $P1A$  initially increases going through a maximum, significantly enough, at filling times approximately equal to its emission time constant. The increase of peak  $P2$  occurs when  $P1A$  starts decreasing. Peak  $P1B$  also goes through a maximum and it contributes to the growth of peak  $P2$  for longer filling times. These general features are common to both irradiated samples. Clearly, this is a case of coupled carrier kinetics with multiple traps. However, note that in contradistinction to mechanisms involving defect relaxation, our results imply that the DOS remains the same and it is the relative occupancies of components that change with time. Any change in energy of a defect would have meant a shift in peak position in TATS, corresponding to a change in time constant of emission, rather than the intensity of the peaks.

There are *a priori* many possible mechanisms that can lead to such a coupling, viz., multiple charge states of the same defect, internal conversion from a metastable to stable state, or even some more elaborate defect relaxation process. In the present case, the key observation is that the shallower states lose charges to the deeper ones, when filling times are larger than their characteristic emission time. This suggests redistribution of charges through multiple trapping. For filling times ( $t_f$ ) shorter than the  $\tau_e$  of a particular level, the occupancy increases in proportion to the product of its capture constant and number density of empty states. For  $t_f > \tau_e$ , emitted electrons from a shallow trap are recaptured by deeper states with an increase in filling time. The situation can be modeled using the following rate equations for independent traps:

$$\frac{dn_{Ti}}{dt} = -e_i n_{Ti} + c_i n (N_{Ti} - n_{Ti}), \quad i = 1 \text{ to } m \quad (3)$$

with a crucial constraint on the concentration of electrons as  $n = \sum_{i=1}^m (N_{Ti} - n_{Ti})$ , where  $n_{Ti}$  is the concentration of occupied states for the  $i$ th level with  $e_i$  and  $c_i$  its emission rate and capture constants and  $N_{Ti}$  its total concentration. We have numerically solved the above set of equations with  $m = 3$  using model parameters for  $N_{Ti}$  and  $c_i$  and experimental

emission time constants, and are able to reproduce the observed features of Fig. 4. Note that, although the intermediate level  $P1B$  participates in the process of charge redistribution, its peak occupancy occurs for filling time larger than its emission time constant. This may be due to field enhancement of emission rate during the transient.

A necessary condition for the observation of redistribution of electrons through the conduction band is that the number of trapping sites available be much larger than the number of electrons available for capture. This condition is clearly satisfied in our experiment for large damage since such damaged regions are highly compensated. The change in charges in the compensated region is reflected in the width of the depletion layer, whose edge lies in the undamaged region. This allows convenient use of standard high-frequency capacitance measurements to monitor charge relaxation in this region is reduced to near intrinsic levels and hence the dynamic time scale is slowed down varying in the range from milliseconds to seconds, enabling convenient observation of the charge redistribution effect.

Charge redistribution among multiple traps has been observed in the case of silicon related  $DX$  centers in  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ .<sup>14</sup> However, the dynamics is more complicated in that case due to the specific model of local alloy disorder, in which the same donor atom relaxes in a variety of local environments with distinct energy levels. In the case of hydrogenated  $a$ -Si, model distinction was difficult since both the model of Cohen *et al.*<sup>1</sup> and the model of Farmer and Su<sup>2</sup> used convolution with a broad density of states. Our results unambiguously confirm that it is not necessary to invoke hierarchical relaxation to explain progressive deepening of energy levels leading to slowing down of emission transients with filling time. In our study we have been able to simulate conditions of those experiments without going over to the amorphization regime, and thus we avoided the complexity of having to deal with any particular level distribution.

Note that the fully developed  $P2$  peak required a Gaussian broadening with FWHM of 25 meV [see Fig. 3(e)]. On the other hand, no significant broadening was observed for the same level in the sample irradiated with the lower dose. This broadening therefore is a measure of inhomogeneities or disorder in the environment of the defects. It would require a more detailed study to track this level of broadening along with a possible increase in multiplicity of levels to the full amorphization limit. It is important to point out the central role that a careful choice of spectroscopy plays in distinguishing between these two different effects of disorder, i.e., multiple defects and disorder broadening. The mean emission energy is the result of a high degree of localization provided by the short range part of the defect potential, whereas its broadening can be viewed as resulting from the long, possibly Coulombic tail of the potential, which samples a much larger volume. The existence of this broadening in our spectra for the high dose sample can be considered as a *post facto* confirmation that we are indeed in the high disorder limit.

From Arrhenius analysis of the CC-TATS signal, the defect level corresponding to peak  $P1B$  is found to be located at  $E_c - 0.42 \text{ eV}$  with a capture cross section of  $\sim 3 \times 10^{-15} \text{ cm}^2$ . It is commonly attributed to a single nega-

tively charged state of the divacancy  $V_2$ . In most DLTS studies, it is reported to appear along with an overlapping peak due to the phosphorus-vacancy complex ( $E$  center). The peaks  $P1A$  and  $P1B$  may be due to similar nearly overlapping peaks, and resolvability as demonstrated here would facilitate their further study. It is interesting to note that effects such as motional averaging of two configurations and sensitivity to damaged related strain have been invoked to explain DLTS line shapes of the  $V_2$ -related peak.<sup>13</sup> The peak  $P2$  has an energy level of  $E_c - 0.5$  eV and capture cross section of  $8 \times 10^{-16}$  cm<sup>2</sup> as obtained from Arrhenius analysis. Other electrical measurements show that the defect is primarily responsible for compensation in the damaged layer.<sup>15</sup> Mention of a similar midgap level has sporadically been found in the literature without any proper identification.<sup>16</sup> It is tempting to attribute it to dangling bonds in this nearly amorphized material and treat it as precursor of the  $D$  states in amorphous silicon.<sup>17</sup> Such a conclusion has to wait until it is possible to have a sufficient

number of spins in the damaged layer so as to enable an electron paramagnetic resonance (EPR) study on the same samples on which electrical studies are carried out. From our preliminary electrical studies, it appears to be due to higher order complexes of mobile interstitials,<sup>10,15</sup> which may in turn give rise to dangling bonds.

In summary, we have studied charge relaxation in severely damaged regions in silicon by embedding them in the depletion layer of otherwise crystalline material. Multiple trap levels, which have moderate broadening of energy for heavy damage, have been resolved. We have provided unambiguous transient-based spectroscopic evidence of charge redistribution among multiple levels. In the light of our results, the need to invoke novel hierarchical defect relaxation mechanisms to explain the progressive slowing down of charge-relaxation transients in disordered silicon must be re-examined.

We thank Dr. V. A. Singh for a critical reading of the manuscript.

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