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New vacancy-related defects in *n*-type silicon

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Using deep-level transient capacitance spectroscopy, four dominant vacancy-related defects are found to be produced by room-temperature 2.5-MeV electron irradiation of *n*-type (phosphorus concentration $\sim 10^{16}$ cm^{-3}) floating-zone silicon. This is in contradiction to the simple accepted model of vacancy trapping to produce predominantly oxygen- and phosphorus-vacancy pairs. We observe the oxygen-vacancy pair, but we now have two candidates for the phosphorus-vacancy pair. One of these displays properties suggestive of configurational metastability with four distinct configurations. We suggest that the remaining defect could be a vacancy-unknown impurity pair (carbon ?) or possibly the isolated lattice vacancy in a new, more stable configuration.

INTRODUCTION

A simple model for the formation of electrically active centers by high-energy electron bombardment of phosphorus-doped silicon has evolved from electron paramagnetic resonance (EPR) studies:[1] The primary defects are vacancies and silicon interstitials. Vacancies migrate and combine primarily with either substitutional phosphorus to produce phosphorus-vacancy pairs[2] ($P \cdot V$) or with oxygen to form oxygen-vacancy pairs[3] ($O \cdot V$). These have been associated with electron traps with energy levels[4] at 0.44 and 0.17 eV, respectively, as shown by a variety of techniques[3,5] including deep-level transient capacitance spectroscopy[6] (DLTS) and thermally stimulated capacitance spectroscopy (TSCAP).[7] The role of interstitials is less clear except for the assignment of a level at ~ 0.10 eV to carbon interstitials[8,9] formed by the displacement of substitutional carbon impurities by mobile silicon interstitials.

The results we present here appear to contradict this simple model. In a DLTS study, we observe four distinct vacancy-related defects of comparable concentration that are produced by room-temperature electron irradiation in phosphorus-doped floating-zone silicon. One of these is associated with the level at 0.10 eV which we conclude was previously incorrectly identified with interstitial carbon. Another displays a remarkable multistability which we postulate arises from four distinct configurations for the defect that can be frozen in and studied separately. In this preliminary report we cannot as yet provide unambiguous identification of the different defects. The information is sufficient, however, to allow some provocative speculations which should stimulate further investigations.

EXPERIMENT

The samples were prepared from Monex floating-zone *n*-type wafers (phosphorus concentration $\sim 8\times10^{15}$ cm^{-3}). To avoid excess oxygen incorporation, p^+n junction diodes were fabricated by implanting boron to a depth of ~ 0.3 μm (80 keV, 1.4×10^{14} atoms/cm^2) with a subsequent anneal in a N_2 atmosphere for 20 min at 850 °C. For each experiment, two or three diodes were mounted on a single TO-5 header so that different biases could be applied to the diodes under identical annealing conditions.

Electron irradiations were performed at 2.5 MeV with the external beam from a 3-MeV Van de Graaff accelerator. The samples were mounted on an air-cooled aluminum block. Typical irradiation dosages were 1.5×10^{16} or 3.0×10^{16} e/cm^2.

The diodes were studied by DLTS with an apparatus similar to that described by Lang.[10] Minority-carrier injection was supplied by applying forward bias to the diodes. Our procedure was to warm the samples to the prescribed temperature, inject for 5 min at 2.5 A/cm^2, and then cool with the appropriate bias to 77 or 50 K and initiate the DLTS scan. All DLTS scans were performed with increasing temperature. The electrical level positions quoted for the new DLTS peaks were determined in the conventional manner by combining scans with several different rate windows, with a $2kT$ correction factor to account for the combined temperature dependences of the free-carrier thermal velocity and the density of conduction-band states. Capture cross sections were not determined, and additional possible corrections for their temperature dependences are not included.

RESULTS

Room-temperature irradiation produces the DLTS spectrum shown in Fig. 1(a). There are strong peaks corresponding to levels at 0.10, 0.26, and 0.44 eV, and a weak peak at 0.17 eV. In previous studies, the levels at 0.17 and 0.44 eV were concluded to arise from O·V and P·V pairs, respectively.[6,7] The 0.10-eV level anneals out quickly at 350 K, as shown in Fig. 1(b), or more slowly at room temperature ($\sim$295 K). The room-temperature annealing curve is shown in Fig. 2.

It was this instability of the 0.10-eV level[12] that led to its previous assignment to interstitial carbon,[8] which also anneals in this temperature range.[13] However, the results of Fig. 2 strongly suggest that this association was incorrect. The 0.17- and 0.44-eV centers grow in close 1:1 correspondence with the disappearance of the 0.10-eV level. The sum of the intensities of all of the peaks remains approximately constant. We propose, therefore, that the 0.10-eV defect is vacancy related, and the annealing process simply involves redistribution of vacancies between different traps. We measure the kinetics of the annealing process to be first order, with a characteristic time constant τ given by

$$\tau^{-1} = (5\times 10^{7})\exp(-0.72\ \text{eV}/kT)\ \text{sec}^{-1}\ . \qquad (1)$$

(This rate is for zero bias on the diode. The rate with reverse bias is about a factor of 2 slower but with approximately the same activation energy.) These annealing kinetics agree closely with those determined in the earlier studies,[8] confirming that the same defect is being studied.

If the sample is now subjected to minority-carrier injection at $T \geq 240$ K, several new centers are observed. In Fig. 1(c) we show the spectrum after 240-K injection and cooling under zero-bias conditions. A decrease in the 0.44-eV peak is accompanied by the emergence of new peaks at 0.23 and 0.34 eV. Continuing this injection procedure at increasing temperature produces further changes, as summarized in Fig. 3. The 0.26 level reemerges, as does eventually the 0.10 level, which, in turn, as it anneals, converts to more 0.17-eV defects. Again, the total concentration of defects remains approximately constant.

If we do not inject above 280 K, we find that we can cycle reversibly between the four levels at 0.23, 0.26, 0.34, and a level at 0.44 eV which contributes partially to the total intensity of the 0.44-eV peak. This is accomplished by dif-

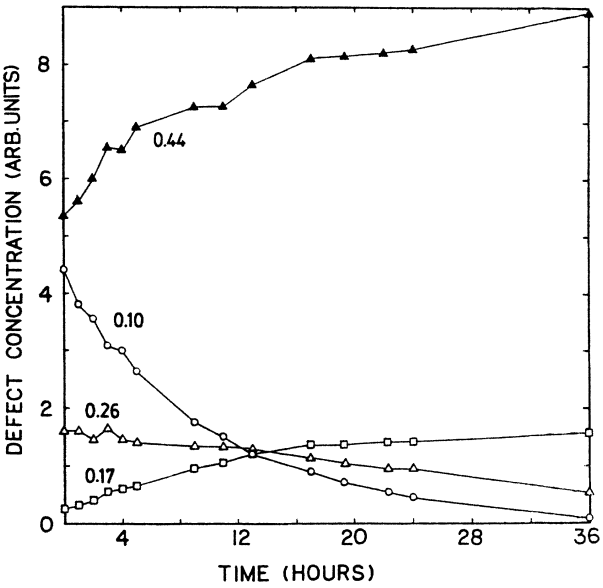

FIG. 2. Defect concentration during isothermal annealing at 295 K following room-temperature irradiation, determined from DLTS peak heights. The amplitudes have been corrected for the presence of small peaks at 0.23 and 0.39 eV due to the divacancy (Ref. 11).

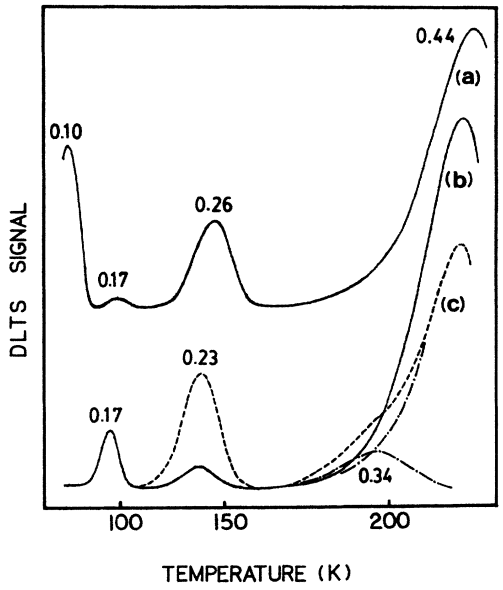

FIG. 1. DLTS spectra (rate window: 22.6 sec^{-1}). (a) Immediately after room-temperature irradiation. (b) After annealing 30 min at 350 K (——). The 0.10- and 0.26-eV centers have converted to the 0.17- and 0.44-eV centers. (c) After 240-K injection for 5 min (– – –). The 0.44-eV center has decreased and new peaks at 0.34 and 0.23 eV have emerged. The – · – · lines show the 0.34-eV peak after subtracting out the 0.44-eV peak.

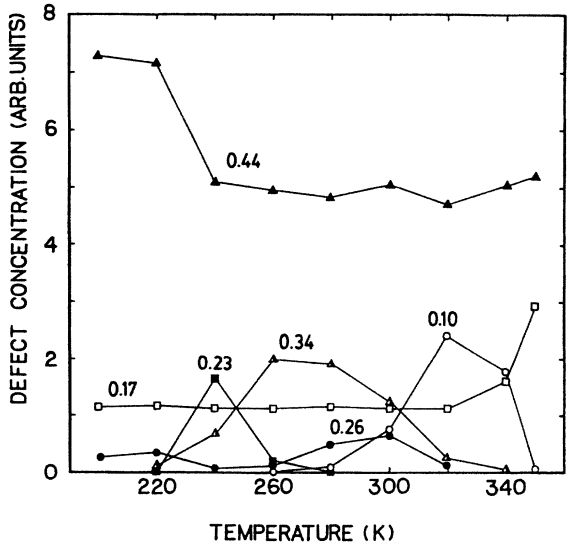

FIG. 3. Defect concentration after injection annealing at each temperature for 5 min determined as in Fig. 2.

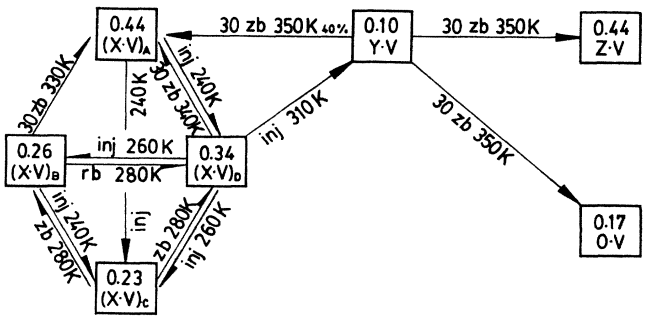

FIG. 4. Conditions for interconversion between the vacancy-related centers: (i) inj (T); forward bias injection (2.5 A/cm^2) for 5 min at T followed by cooling with zero bias to 80 K. (ii) 30 zb (T); zero-bias annealing for 30 min at T followed by cooling with zero-bias to 80 K. (iii) zb (T); zero-bias cooling from T to 80 K. (iv) rb (T); reverse bias (5V) cooling from T to 80 K.

ferent combinations of injection, temperature, and/or bias conditions upon cooling. Some of the conditions for cycling between these levels are shown in Fig. 4. The sum of the intensities from these four peaks remains constant through many cycles, with no apparent change in the intensities of the other DLTS peaks. If vacancies were migrating through the lattice during these conversions, then interactions with other impurities are also possible and would result in the alteration of other DLTS peaks. This suggests that these four peaks arise from a *single defect* which has four distinct configurations which can be frozen in depending upon charge state, temperature, etc.[14] Consistent with this interpretation, we tentatively label them $(X\cdot V)_A$, $(X\cdot V)_B$, $(X\cdot V)_C$, and $(X\cdot V)_D$ to denote a vacancy pair with a common trap X.

Under normal thermal annealing (30 min, zero bias) the $X\cdot V$ centers are stable until ~ 400 K, where they anneal out irreversibly accompanied by generation of the 0.17-eV center. After this stage no bias or temperature conditions have been found in which we can recover either the $X\cdot V$ centers or the 0.10-eV center. The remaining 0.44-eV peak, which we label $Z\cdot V$, anneals out (30 min, zero bias) at ~ 450 K.

As noted in Fig. 3, the 0.10-eV center can be regenerated from the $X\cdot V$ center by injection at $T > 300$ K. Once regenerated, the 0.10-eV center shows the same thermal annealing behavior (no injection) as when first formed by irradiation. This is also indicated in Fig. 4. Some of the intensity ($\sim 40\%$) goes to the 0.44-eV ($X\cdot V$) center, and the remainder is divided between the 0.17-eV level and the irreversible part of the 0.44-eV ($Z\cdot V$) level. Continued cycling involving the 0.10-eV center eventually results in all of the centers being converted into $Z\cdot V$ and the 0.17-eV center. Again, the total concentration of centers remains approximately constant. Consistent with our conclusion that the 0.10-eV level is vacancy related, we have labeled it $Y\cdot V$ in Fig. 4.

DISCUSSION

These results demonstrate that vacancy interactions can be considerably more complex than previously thought. In our samples there appear to be at least four important distinct defects involving a single vacancy produced by room-temperature electron irradiation.

We detect only one level at 0.17 eV, which we assume therefore is correctly identified with the $O\cdot V$ pair. We now have two defects, however, $X\cdot V$ and $Z\cdot V$, either of which might be associated with the $P\cdot V$ pair. Both give rise to a level at 0.44 eV and anneal in the general temperature region (~ 150 °C) estimated from EPR studies of the $P\cdot V$ pair. In previous DLTS (Ref. 15) and electrical measurement studies,[16,17] it was concluded that the higher-temperature stage (our $Z\cdot V$) matches best the EPR results for $P\cdot V$. However, detailed annealing kinetics have not been reported for EPR studies, and this conclusion must therefore be taken with some caution. Monitoring the total capacitance of our diodes indicates that both $X\cdot V$ and $Z\cdot V$ may involve phosphorus, consistent with the conclusion of an early electrical measurement study.[16]

$X\cdot V$ shows a remarkable multistability, cycling reversibly between states of 0.44, 0.34, 0.26, and 0.23 eV. *Bi*stability has recently been discovered for several defects in InP (Refs. 18–20) and Si (Refs. 21–23), and is a topic of great current interest. To our knowledge, the present observation of *four* distinct states is unique. This behavior is suggestive of a vacancy-defect complex where the particular local arrangement of its constituents is determined by its stability versus charge state, temperature, and activation barrier for conversion. Such effects have already been postulated for iron-acceptor pairs[24] and $B\cdot V$ pairs[22,23] in silicon, where two configurations detected by capacitance studies were assigned to nearest and next-nearest pair separations.

The $Y\cdot V$ defect, giving rise to the 0.10-eV level, is another interesting center. The 10^8 preexponential factor of the annealing kinetics strongly suggests long-range migration of a defect ($\sim 10^5$ steps as an entity, occurring at a rate of $\sim 10^{13}$ s^{-1}). This, in turn, suggests two intriguing possibilities.

(1) Y is an impurity. The only background impurity besides oxygen known to be universally present in significant concentration in silicon is carbon. Migration of a carbon-vacancy pair as an entity would produce $P\cdot V$ and $O\cdot V$ pairs which incorporate a carbon atom as a constituent. The dominant $P\cdot V$ defect studied by EPR (Ref. 2) displayed easy reorientation between equivalent Jahn-Teller distortions, which is inconsistent with the presence of an additional impurity which would lower the symmetry. However, it is interesting to note that an additional $P\cdot V$ defect was also reported in these early studies that did not display these reorientations.[2]

(2) Y is not an impurity, the 0.10 level arising from the *isolated* vacancy. This would explain naturally its generation from the breakup of the $X\cdot V$ pairs and its long-range migration to form $P\cdot V$ and $O\cdot V$ pairs. It seems to conflict, however, with the unambiguous observation of long-range migration of vacancies at ~ 77 K in low-temperature irradiated materials. It might be a less-mobile higher-stability configuration of the vacancy, presumbly self-trapped over a barrier too high to be surmounted at cryogenic temperatures. Such behavior has been postulated previously for the vacancy in a different context.[25]

In conclusion, these studies have raised a number of important new questions concerning the properties of vacancies and their interactions in silicon. These questions will probably only be answered by detailed correlative studies using EPR. We are currently initiating such studies.

ACKNOWLEDGMENTS

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[1]G. D. Watkins, in *Defects and Their Structure in Non-Metallic Solids,* edited by B. Henderson and A. E. Hughes (Plenum, London, 1976), p. 203.

[2]G. D. Watkins and J. W. Corbett, Phys. Rev. **134**, A1359 (1964).

[3]G. D. Watkins and J. W. Corbett, Phys. Rev. **121**, 1001 (1961).

[4]Energy levels given in this paper are the energy differences in electron volts between the electron traps and the conduction-band edge.

[5]G. D. Watkins, J. W. Corbett, and R. M. Walker, J. Appl. Phys. **30**, 1198 (1959).

[6]L. C. Kimerling, in *Radiation Effects in Semiconductors, 1976,* IOP Conf. Ser. No. 31, edited by B. Urli and J. W. Corbett (IOP, London, 1977), p. 221.

[7]J. W. Walker and C. T. Sah, Phys. Rev. B **7**, 4587 (1973).

[8]L. C. Kimerling, P. Blood, and W. M. Gibson, in *Defects and Radiation Effects in Semiconductors, 1978,* IOP Conf. Ser. No. 46, edited by J. H. Albany (IOP, London, 1979), p. 273.

[9]R. D. Harris and G. D. Watkins, in *Proceedings of the Thirteenth International Conference on Defects in Semiconductors,* edited by L. C. Kimerling and J. M. Parsey, Jr. (AIME, New York, 1985), p. 799.

[10]D. V. Lang, J. Appl. Phys. **45**, 3023 (1974).

[11]A. O. Evwaraye and E. Sun, J. Appl. Phys. **47**, 3776 (1976).

[12]In Ref. 8 the level was reported to be at 0.12 eV. In Ref. 9, it was reported to be 0.09 eV. Our results indicate 0.10 eV. Such variations are common in DLTS studies reported by different workers and reflect primarily the difficulty of accurate temperature determination in these measurements.

[13]G. D. Watkins and K. L. Brower, Phys. Rev. Lett. **36**, 1329 (1976).

[14]We acknowledge helpful discussions with A. Chantre who informs us that he also has observed metastable effects involving the 0.44-eV level. We thank him in particular for the important suggestion that the complex behavior we have observed under injection (Fig. 3) could be associated with such effects.

[15]L. C. Kimerling, H. M. DeAngelis, and J. W. Diebold, Solid State Commun. **16**, 171 (1975).

[16]M. Hirata, M. Hirata, and H. Saito, J. Appl. Phys. **37**, 1867 (1966).

[17]L. C. Kimerling, H. M. DeAngelis, and C. P. Carnes, Phys. Rev. B **3**, 427 (1971).

[18]M. Levinson, J. L. Benton, and L. C. Kimerling, Phys. Rev. B **27**, 6216 (1983).

[19]M. Levinson, M. Stavola, J. L. Benton, and L. C. Kimerling, Phys. Rev. B **28**, 5848 (1983).

[20]M. Stavola, M. Levinson, J. L. Benton, and L. C. Kimerling, Phys. Rev. B **30**, 832 (1984).

[21]G. E. Jellison, Jr., J. Appl. Phys. **53**, 5715 (1982).

[22]S. K. Bains and P. C. Banbury, J. Phys. C **18**, L109 (1985).

[23]A. Chantre, Phys. Rev. B **32**, 3687 (1985).

[24]A. Chantre and D. Bois, Phys. Rev. B **31**, 7979 (1985).

[25]A. Seeger and K. P. Chik, Phys. Status Solidi **29**, 455 (1968).