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Annealing Studies of Defects Pertinent to Radiation Damage in Si:B

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Annealing studies are made of liquid nitrogen electron irradiation-induced defects in p-type silicon. The signal from the carbon interstitial (C_I) is observed to anneal away more rapidly in pulled than in float-zone silicon. This peculiarity of the C_I annealing behaviour is tentatively attributed to the difference in the oxygen content between the two materials. The properties of some other levels are reported as well.

Es werden Ausheiluntersuchungen von elektronenstrahlinduzierten Defekten (Temperatur des flüssigen Stickstoffs) in p-leitendem Silizium durchgeführt. Es wird beobachtet, daß das Signal vom Zwischengitterkohlenstoff (C_I) schneller in aus der Schmelze gezogenem als aus zonengeschmolzenem Silizium ausheilt. Diese Besonderheit des C_I-Ausheilverhaltens wird dem Unterschied im Sauerstoffgehalt zwischen beiden Materialien zugeschrieben. Die Eigenschaften einiger anderer Niveaus werden ebenfalls mitgeteilt.

1. Introduction

The energy states and the properties of defects pertinent to electron irradiation damage of Si:B at 80 K have been reported recently [1, 2] by using DLTS (deep-level transient spectroscopy) measurements. As a continuation of this work we made annealing experiments to study the thermal stability of some of these states. It is obvious that any information pertaining to this matter is very useful for a better understanding of the behaviour of the defects. In an earlier paper [3] it has been reported that a peak, produced after room temperature irradiation and attributed to the $E_v + 0.28$ eV level of the C_I, disappears with increasing temperature more quickly in pulled than in float-zone material. A close parallel exists between those results and our present observations.

In the presentation of the defect states here we have adopted a labelling system by using a prefix H for the hole traps or E for the electron traps followed by a number in brackets indicating the energy depth in eV from the valence or the conduction band, respectively. The electrical levels quoted for the peaks were determined without the $2kT$ correction. From here on fz stands for float-zone and p for pulled silicon.

2. Experimental

Schottky diodes were fabricated either from fz (6.4—7.4 Ωcm) or from p (3—5 Ωcm) silicon wafers. The preparation procedure has been reported elsewhere [3]. C–U profiling of the junctions revealed uniform active layer concentrations of $2.2 \times \times 10^{15}$ cm^{-3} for the fz and 3.8×10^{15} cm^{-3} for the p material, on the average. Preliminary DLTS characterization revealed no observable defect states.

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Electron irradiations were performed in situ at 1.5 MeV with the external beam from a 2 MeV Van der Graaf accelerator. The samples were subjected to beam currents in the range of 0.15 to 0.33 $\mu A/cm^2$ and doses $(1.7 \text{ to } 3.5) \times 10^{16}$ e^-/cm^2. The temperature of irradiation was 80 K.

Transient capacitance measurements were carried out by using a standard DLTS experimental set-up [4]. The DLTS technique, due to its unsurpassed sensitivity, has been proved a very effective tool in monitoring the variations of peak heights as a function of heat treatment.

The annealings were carried out under zero bias conditions at temperatures below 500 K (above this temperature our Schottky barriers were destroyed).

3. Results and Discussion

The results derived from deep level measurements of low temperature irradiated boron-doped silicon with the temperature cycling in the range from 80 to 300 K are already known [1, 2]. A peak $E_v + 0.28$ eV attributed to the C_I has been observed to diminish from 295 K upwards in p silicon. In fz silicon, however, similar decreases of the amplitude of the C_I peak have been observed from temperatures slightly higher than 295 K. Moreover, the diminution of the C_I signal in the latter kind of material has been observed to slow down substantially.

Moreover, the disappearance of the C_I signal in p Si produced in room temperature irradiation occurs very rapidly. We can detect it clearly in the course of successive scans [3]. The length of time for the completion of the phenomenon is less than that required for the disappearance of the C_I peak produced by irradiation at 80 K. It may be argued that during the irradiation and due to it, the temperature of the specimens was slightly larger than 300 K and thus the produced C_I atoms became mobile and diffused in the crystal lattice. However the defect created in fz specimens irradiated under the same conditions did not show a similar behaviour. We should recognize that the results reveal an underlying reality which suggests a unique role for the oxygen impurity in the silicon lattice. We shall defer this discussion for later.

In another experiment of liquid nitrogen irradiation we avoided to leave the samples at room temperature. We performed, instead, annealings at 470 K for 90 min. The obtained DLTS spectra are depicted in Fig. 1 and 2 for the fz and p silicon, respectively. The serial number which characterizes every peak in those figures has been taken from Table 1, where for the sake of completion, we have summarized all the trap states appearing in the spectra during the above measurements.

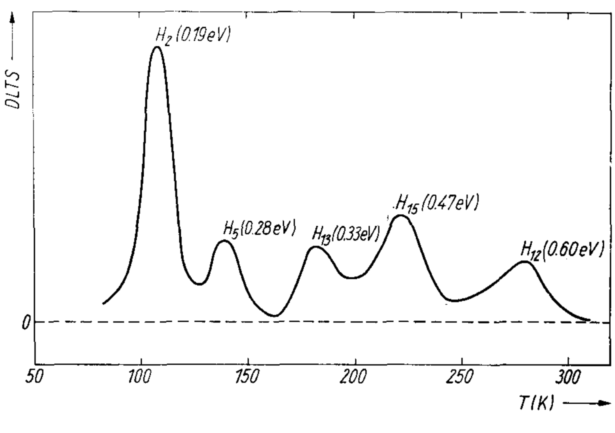

Fig. 1. The DLTS spectrum of float-zone Si:B, $p = (6.4-7.4$ Ω cm), 1.5 MeV electron irradiated at 80 K to a dose of $\approx 1.7 \times 10^{16}$ e^-/cm^2 and a beam current of ≈ 0.15 $\mu A/cm^2$, after an anneal at 470 K for 90 min (rate window = 5 s^{-1})

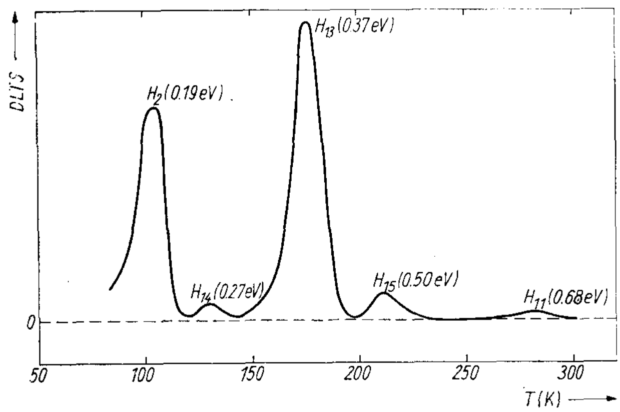

Fig. 2. The DLTS spectrum of pulled Si:B, $p = (3 - 5\,\Omega\,\text{cm})$, 1.5 MeV electron irradiated at 80 K to a dose of $\approx 3.5 \times 10^{16}\,e^-/\text{cm}^2$ and a beam current of $\approx 0.33\,\mu\text{A/cm}^2$, after an anneal at 470 K for 90 min (rate window $= 5\,\text{s}^{-1}$)

Table 1

Summary of defects in boron-doped, electron-irradiated S_i at 80 K

state	activation energies fz	activation energies p	other information	identity
H_1	$E_1 < E_v + 0.13$ eV			V
H_2	$E_v + 0.19$ eV		H_2 and H_3 form in p silicon under conditions of irradiation	V_2
H_3		$E_v + 0.15$ eV	(dose $= 3.5 \times 10^{16}\,e^-/\text{cm}^2$, $i = 0.33\,\mu\text{A/cm}^2$) [2]	V_2-related ,
H_4		$E_v + 0.13$ eV	H_4 forms in p silicon.under conditions of irradiation (dose $= 1.7 \times 10^{16}\,e^-/\text{cm}^2$, $i = 0.15\,\mu\text{A/c,m}^2$) [11]	V_2-related
H_5	$E_v + 0.28$ eV			C_I
H_6	$E_v + 0.31$ eV		H_6, H_7 belong to the one configuration and H_8 to the other configuration of a bistable defect [1]	B_s–V
H_7	$E_v + 0.38$ eV			B_s–V
H_8	$E_8 < E_1$			B_s–V
H_9		$E_v + 0.34$ eV	charge-dependent peak amplitudes [11]	V-related
H_{10}		$E_v + 0.38$ eV		?
H_{11}		$E_v + 0.68$ eV		?
H_{12}	$E_v + 0.60$ eV			?
H_{13}	$E_v + 0.33$ eV	$E_v + 0.37$ eV		C_i–C_s or C–O–V or both
H_{14}		$E_v + 0.27$ eV		B–O–V
H_{15}	$E_v + 0.47$ eV	$E_v + 0.50$ eV		?
E_1	$E_c - 0.17$ eV			V–O
E_2		$E_c - 0.25$ eV		B_i–O_i or V_2 or both
E_3	$E_c - 0.36$ eV			?
E_4	$E_c - 0.46$ eV			V_2 or C–O–V_2

The C_I signal has been seen in both materials to diminish while another signal about 0.35 eV above the valence band grows. It is surprising, however, that the C_I peak persists in the fz silicon where it does not disappear completely in contrast with previous results [5, 6]. It has been reported in particular that in vacuum-floating-zone-refined Si:B, specially doped with carbon (10^{17} cm^{-3}) the Si-G_{12} EPR spectrum of the C_I disappears with a time constant of 30 min. In our experiments, however, C_I retains considerable concentration in spite of a heat treatment at a higher temperature for a longer time duration.

We are inclined to believe that physical reasons must cause the difference in the annealing behaviour of the C_I between the two kinds of silicon. The content of the dopant impurity is of the same order in both materials. Carbon also should have the same concentration in the two materials. Therefore, the interstitially incorporated oxygen impurity (10^{16} cm^{-3} in fz and 10^{18} cm^{-3} in p) appears as a strong candidate for causing the phenomenon. From the theoretical point of view the physical origin of the phenomenon could be basically understood on the grounds of lattice deformation due to the oxygen impurity. It is generally accepted that interstitial impurities like oxygen always expand the silicon lattice [7]. This distortion should be larger in p silicon and may lead to changes in the migration energy and the annealing temperature of the C_I atoms. Thus the annealing kinetics of the C_I is affected. In other words, an annealing at a high temperature may cause a faster disappearance of the C_I peak in p than in fz silicon. However, to the best of our knowledge, there is practically a lack of data in the literature concerning the effect of lattice distortions from incorporated impurities on the annealing processes of radiation damage in silicon. Aside from this, we feel that the above explanation may not be adequate to account for the observed difference in the annealing behaviour of the C_I. In search for other possible mechanisms which may cause the phenomenon or contribute to some extent in its appearance one should consider interactions with oxygen. The presence of oxygen in the substrate was found to influence directly the annealing behaviour of the radiation damage in silicon [8]. It is obvious that the validity of the above speculations remain in question until detailed data become available.

The H_{14} (0.27 eV) level seen only in p material may be considered as an oxygen associated defect, probably the (B–O–V) complex. The mechanism of its production is based on the dissociation of the (B_i–O_i) pair responsible for the E (0.26 eV) level. The liberated mobile boron interstitial is captured by a multivacancy–oxygen complex in agreement with previous reports [3, 9, 10]. In an earlier work [11] where similar p specimens were subjected to a dose of $\approx 1.7 \times 10^{16}$ e$^-$/cm^2 and a beam current of ≈ 0.15 μA/cm^2 the signal from the H_{14} (0.27 eV) level was so faint that we omitted to report it. We have ascribed its absence to the competitive presence of the carbon impurity which suppresses the creation of boron interstitials. We are disposed to think that the growth of the H_{14} (0.27 eV) level depends on the conditions of irradiation. In a previous experiment [12] on room temperature electron irradiated, edge-defined, film-fed grown ribbon silicon this level emerged even before annealing at 430 K in the heaviest bombarded specimens (fluence $= 10^{16}$ cm^{-2}). Kimerling also [13] did not observe the peak from the E (0.26 eV) level of the (B_i–O_i) pair by irradiating specimens of comparably doped material with 1 MeV electrons but only with electrons of energy in the range of 10 MeV.

It is worth noticing that although the H_{14} (0.27 eV) level has about the same energy as H_5 (0.28 eV), the peak from the latter appears in the spectrum at higher temperatures than that of the first when the same rate window is operated. This means that the capture cross-section of the (B–O–V) complex should be larger than that of the C_I.

The level H_{15} (0.47 eV) in fz material has been also detected in room temperature irradiated specimens subjected to a similar heat treatment [3]. However, in the latter case another level with energy H (0.52 eV) has disappeared during the annealing process.

Allowing for the experimental error in the determination of the activation energies of the defects the two levels, H_{15} (0.47 eV) in the fz and H_{15} (0.50 eV) in the p material, which emerged after identical heat treatment, may have the same origin. It is worth noticing that a level H (0.48 eV) has been observed in Al-doped, pulled silicon electron irradiated at room temperature to emerge only after an anneal at 100 °C [14].

A deep donor level $E_v + 0.45$ eV has also been reported [8] after electrical measurements on p-type silicon, irrespective of the type of acceptor. Its nature was correlated to vacancy-group III impurity centres. After a heat treatment for 50 min at 475 °C a level $E_v + 0.46$ eV has been also seen to emerge in the process of annealing [15] in carbon-implanted, boron-doped silicon. It has also been detected in arsenic- and antimony-implanted silicon.

The H_{12} (0.60 eV) level seen in our low temperature irradiated silicon studies to emerge in the spectrum at least from 250 K upwards [1, 16] should be different from a level of similar energy forming in room temperature irradiated silicon after a heat treatment at 450 K [3]. We should also notice the fact that the H_{12} (0.60 eV) signal seems to increase simultaneously with the annealing away of the B_s–V pair at around room temperature which may give a correlation of the right sense here.

The level H_{11} (0.68 eV) was observed only in the p material and is thermally stable during the afore-mentioned heat treatment. It is difficult to correlate it closely with any previously identified structure. Nevertheless, its energy position in the middle of the gap and its thermal stability may indicate links to the minority centre E_4 (0.46 eV) seen in these studies.

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References

[1] S. K. Bains and P. C. Banbury, J. Phys. C **18**, L109 (1985).
[2] C. A. Londos, J. Phys. Chem. Solids **47**, 1147 (1986).
[3] C. A. Londos, phys. stat. sol. (a) **92**, 609 (1985).
[4] D. V. Lang, J. appl. Phys. **45**, 3023 (1977).
[5] Y. H. Lee, L. J. Cheng, J. D. Gerson, P. M. Mooney, and J. W. Corbett, Solid State Commun. **21**, 109 (1977).
[6] G. D. Watkins and K. L. Brower, Phys. Rev. Letters **36**, 1329 (1976).
[7] J. R. Carruthers, R. B. Hoffman, and J. D. Ashuer, J. appl. Phys. **34**, 3389 (1963).
[8] V. S. Vavilov, B. N. Mukashev, and A. V. Spitsyn, Inst. Phys. Conf. Series No. **16**, 284 (1973).
[9] P. M. Mooney, L. J. Cheng, M. Süli, J. D. Gerson, and J. W. Corbett, Phys. Rev. B **15**, 3836 (1977).
[10] M. Roux, J. Bernard, and R. Reulet, J. appl. Phys. **56**, 531 (1986).
[11] C. A. Londos and P. C. Banbury, J. Phys. C **20**, 645 (1987).

[12] A. E. JAWOROWSKI, C. B. PIERCE, S. BURDICK, J. W. CORBETT, and J. I. HANOKA, J. appl. Phys. **52**, 3337 (1981).
[13] L. C. KIMERLING, Inst. Phys. Conf. Series No. **31**, 221 (1977).
[14] Y. H. LEE, K. L. WANG, A. JAWOROWSKI, P. M. MOONEY, L. J. CHENG, and J. W. CORBETT, phys. stat. sol. (a) **57**, 697 (1980).
[15] B. N. MUKASHEV, A. V. SPITSYN, N. FUKUOKA, and H. SAITO, Japan. J. appl. Phys. **21**, 399 (1982).
[16] C. A. LONDOS, Phys. Rev. B **34**, 1310 (1986).

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