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2003 J. Phys.: Condens. Matter 15 S2835

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INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER
J. Phys.: Condens. Matter **15** (2003) S2835–S2842 PII: S0953-8984(03)67280-2

Oxygen-related radiation-induced defects in SiGe alloys

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Received 7 August 2003
Published 19 September 2003
Online at stacks.iop.org/JPhysCM/15/S2835

Abstract
Electronic properties of the vacancy–oxygen (V–O) complex and the interstitial oxygen and carbon atom pair (C_i–O_i) in unstrained $Si_{1-x}Ge_x$ crystals ($0 < x \leqslant 0.06$) have been studied by means of capacitance transient techniques. The $Si_{1-x}Ge_x$ crystals were grown by the Czochralski method and were doped with either phosphorus or boron during growth. The V–O and C_i–O_i centres were introduced into the crystals by room temperature irradiation with 4 MeV electrons or with γ-rays from a ^{60}Co source.

The enthalpy of electron ionization for the single acceptor level of the V–O centre relative to the conduction band edge, ΔH_n, was found to increase with a rate $d(\Delta H_n)/dx = 0.56$ eV upon increase in Ge content. The enthalpy of hole ionization for the single donor level of the C_i–O_i centre relative to the valence band edge, ΔH_p, was found to decrease with a rate $d(\Delta H_p)/dx = -0.96$ eV. For both the V–O- and C_i–O_i-related levels no significant changes in the values of the electron (hole) capture cross section or entropy of ionization with the changes in Ge content were observed. The levels are not pinned to the conduction band edge or to the valence band edge. It is argued that the value of the enthalpy of V–O ionization can be correlated with the lattice parameter or the Si–Si bond length: the larger this parameter, the bigger the enthalpy of the ionization.

1. Introduction

The SiGe alloys are important materials for the future in the microelectronics industry in view of the possibilities of band gap engineering and development of SiGe-based advanced high speed electronic and optoelectronic devices. For the successful fabrication of SiGe-based devices,

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good knowledge of electronic properties of the most abundant lattice defects is required in the whole composition range of SiGe alloys.

The vacancy–oxygen complex (V–O or A centre) and the interstitial oxygen and carbon atom pair (C_i–O_i) are dominant defects induced by irradiation with high energy particles (electrons, protons, etc) in Si crystals grown by the Czochralski method [1, 2]. The structure and electronic properties of the V–O and C_i–O_i defects in Si are well understood [1–5]. The V–O centre is thought to be one of the main radiation-induced defects in oxygen-rich Ge crystals [6, 7]. However, the situation is not so clear as regards the properties of the A centre in Ge crystals although recently some new data have been published [8, 9]. Observations of the C_i–O_i pair in Ge crystals have not been reported. There is little information on the V–O and C_i–O_i complexes in SiGe alloys apart from an article on an infrared absorption study of the V–O centre in electron-irradiated oxygen-rich $Si_{1-x}Ge_x$ crystals [10].

In order to obtain more information on the electronic properties of the vacancy–oxygen and C_i–O_i complexes in $Si_{1-x}Ge_x$ alloys, capacitance transient measurements have been carried out on irradiated oxygen-rich $Si_{1-x}Ge_x$ samples.

2. Experimental details

Samples for this study were prepared from n- and p-type $Si_{1-x}Ge_x$ crystals, which were grown at the Institute of Crystal Growth (Berlin, Germany) by the Czochralski technique [11]. The crystals were doped with either phosphorus or boron during growth. The phosphorus concentration was (1–3) $\times 10^{15}$ cm^{-3}. The boron concentration was (2–5) $\times 10^{15}$ cm^{-3}. The concentrations of interstitial oxygen and substitutional carbon atoms measured by optical absorption were found to be (7–9) $\times 10^{17}$ and (2–3) $\times 10^{16}$ cm^{-3}, respectively. The concentration of Ge in the crystals varied from 1.5 to 6 at.%. The Ge concentration was determined from x-ray diffraction and Raman scattering measurements. Ge-free Si samples with similar concentrations of P, B, O, and C atoms were also studied. The samples were irradiated with 4 MeV electrons or with γ-rays from a ^{60}Co source at room temperature. The sample surfaces were cleaned after the irradiation and Schottky barriers were fabricated by thermal evaporation of Au on n-type samples and by plasma sputtering of Ti on p-type samples. Electronic levels were characterized with conventional deep level transient spectroscopy (DLTS) and high resolution Laplace deep level transient spectroscopy (LDLTS) techniques [12].

3. Experimental results

3.1. Cz-$Si_{1-x}Ge_x$:P

Figure 1 shows DLTS spectra of a Ge-free Si sample and two $Si_{1-x}Ge_x$ samples after irradiation with gamma-rays. A peak with its maximum at about 90–105 K (E_{100}) dominates the spectra of the irradiated samples and a few minor peaks are observed. A brief description of the nature and electronic properties of the E_{100} trap in irradiated $Si_{1-x}Ge_x$ samples has been presented recently in [13]. The E_{100} peak was shown to be related to the vacancy–oxygen complex (V–O or A centre [1, 14, 15]) with a small (<10%) contribution from the interstitial–substitutional carbon pair [16]. It was argued in [13] that in as-irradiated $Si_{1-x}Ge_x$ samples the concentration of the A centres, which have a Ge atom in the first nearest neighbour shell around an off-centre substitutional oxygen atom, is small. Furthermore, it was found that the electronic properties of the V–O complex having a Ge atom in the second nearest neighbour shell as measured by DLTS do not differ significantly ($\Delta E \leqslant 10$ meV) from those for complexes without

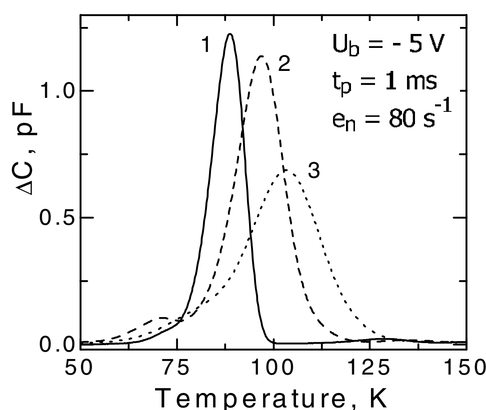

Figure 1. DLTS spectra for gamma-irradiated oxygen-rich n-type $Si_{1-x}Ge_x$ crystals with different Ge content, x (at.%): (1) 0; (2) 2.5; (3) 5.2. The irradiation dose was 230 Mrad. The measurement parameters are presented in the figure.

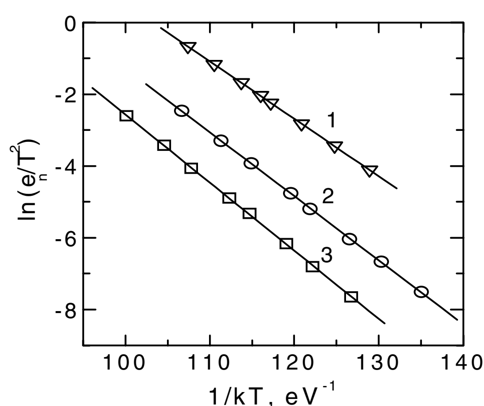

Figure 2. Arrhenius plots of T^2-corrected rates of electron emission from the acceptor level of the V–O complex in gamma-irradiated $Si_{1-x}Ge_x$ crystals with different Ge content, x (at.%): (1) 0; (2) 2.5; (3) 5.2.

Ge atoms as the second nearest neighbours. Therefore, the observed temperature shift of the E_{100} peak maximum in $Si_{1-x}Ge_x$ samples (figure 1) was associated with the changes in electronic properties of the V–O complexes caused by the alteration in the lattice and/or band gap properties of the $Si_{1-x}Ge_x$ alloys with the changes in Ge content.

Figure 2 shows Arrhenius plots of the T^2-corrected rates of emission from the E_{100} trap in irradiated samples with different Ge content. The activation energies for the electron emission, ΔE_n, and pre-exponential factors, A_n, derived from the plots are presented in table 1. The observed changes in emission rates are related mainly to the changes in ΔE_n; the values of the pre-exponential factor are essentially the same. Direct measurements of the electron capture were carried out for the E_{100} trap in irradiated $Si_{1-x}Ge_x$ samples. No significant changes in comparison to the capture process in the Ge-free samples were observed. The capture cross section, σ_n, for the V–O centre exceeds 1×10^{-14} cm^2 in $Si_{1-x}Ge_x$ crystals as well as in Ge-free Si crystals. As the electron capture cross section for the acceptor level of the V–O complex in Si is known to be temperature independent [14], i.e., there is no energy barrier for the capture,

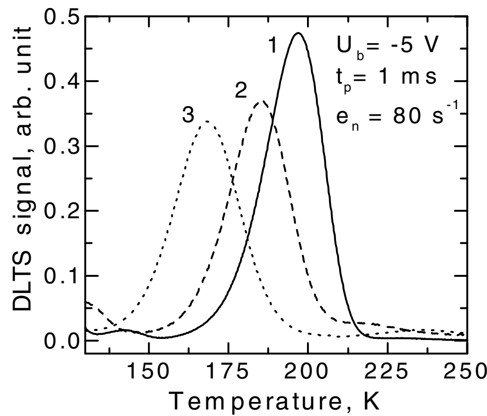

Figure 3. DLTS spectra for electron-irradiated oxygen-rich p-type $Si_{1-x}Ge_x$ crystals with different Ge content, x (at.%): (1) 0; (2) 2.8; (3) 6.0. The irradiation dose was 1.5×10^{15} cm^{-2}. The measurement parameters are presented in the figure.

Table 1. Activation energies and pre-exponential factors of the ionization of the V–O complex in oxygen-rich $Si_{1-x}Ge_x$ crystals, which were irradiated with γ-rays from a ^{60}Co source. The uncertainty in the values of the Ge content is 0.2 at.%. The uncertainties are 0.002 eV for the ΔE_n values and 0.3×10^7 for the A_n values.

Ge content (at.%)	$\Delta E_n = \Delta H_n$ (eV)	A_n (10^7 s^{-1} K^{-2})
0	0.161	1.50
1.5	0.169	1.25
2.0	0.173	1.45
2.6	0.178	1.55
5.2	0.190	1.40

the values determined for ΔE_n for the V–O(−/0)-related level should coincide with the values of enthalpy of the defect ionization, ΔH_n. So, the enthalpy of V–O ionization increases in $Si_{1-x}Ge_x$ alloys with the increase in Ge content. There is no significant change in entropy, ΔS_n, with the changes in Ge content, because the A_n and σ_n values are very similar in the crystals with different Ge content ($A_n \sim \exp(\Delta S_n/k)\sigma_n$).

3.2. Cz-$Si_{1-x}Ge_x$:B

Figure 3 shows conventional DLTS spectra in the temperature range 130–250 K for p-type $Si_{1-x}Ge_x$ samples, which were irradiated with 4 MeV electrons. A peak with its maximum at 170–195 K (H_{190}) dominates the spectra. A dominant DLTS peak similar to the H_{190} one was observed earlier for p-type Cz-Si samples irradiated with high energy particles [17–20]. It seems certain now that this peak is related mainly to the C_i–O_i complex [3, 20, 21], although other unidentified defects were suggested to contribute to the peak [18–20]. We have observed a sharp dominant line in the LDLTS spectra taken in the temperature range 185–210 K for irradiated Ge-free samples. This indicates a mono-exponential transient related to a single well-defined energy level. From an Arrhenius plot of T^2-corrected emission rates (figure 4), the values of activation energy of hole ionization, ΔE_p, and apparent capture cross section, σ_{pa} ($\sigma_{pa} = \sigma_p \exp(\Delta S_p/k)$), were determined as 0.360 eV and 6.5×10^{-16} cm^2 for the H_{190} trap in the Ge-free samples. Beside the LDLTS measurements, direct hole capture

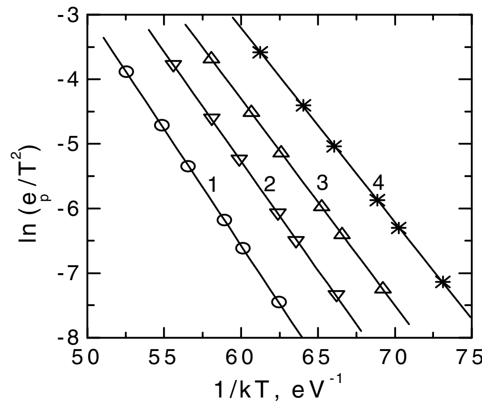

Figure 4. Arrhenius plots of T^2-corrected hole emission rates from the donor level of the C_i–O_i complex in electron-irradiated $Si_{1-x}Ge_x$ crystals with different Ge content, x (at.%): (1) 0; (2) 2.8; (3) 4.4, (4) 6.0.

Table 2. Activation energies and pre-exponential factors of the ionization of the C_i–O_i complex in oxygen-rich $Si_{1-x}Ge_x$ crystals, which were irradiated with 4 MeV electrons. The uncertainty in the values of the Ge content is 0.2 at.%. The uncertainties are 0.002 eV for the ΔE_p values and 0.5×10^6 for the A_p values.

Ge content (at.%)	$\Delta E_p = \Delta H_p$ (eV)	A_p (10^6 s^{-1} K^{-2})
0	0.360	3.3
1.5	0.344	2.85
2.8	0.338	3.3
4.4	0.319	2.8
6.0	0.301	2.8

measurements were carried out for the H_{190} trap in Ge-free samples. The σ_p value was found to be (5–6) $\times 10^{-17}$ cm^2 in the temperature range 190–215 K. The values determined are close to those reported in the literature for the donor level of the C_i–O_i complex [20, 22, 23]. On the basis of the above results the H_{190} peak in irradiated Ge-free samples has been assigned to the C_i–O_i pair. In p-type Cz-Si crystals, which have been studied in the present work, we have observed a contribution from only one dominant trap (C_i–O_i) to the H_{190} peak.

Conventional DLTS spectra of irradiated $Si_{1-x}Ge_x$ resemble that for the Ge-free sample but the H_{190} peak shifts to lower temperature with the increase in Ge content (figure 3). It is thought that Ge impurity atoms do not affect interstitial-related defect reactions in irradiated Si crystals [24, 25]. Bearing this in mind and taking into account the similarity in concentrations of B, O, and C atoms in the Ge-free and Ge-rich p-type crystals studied, it is reasonable to suggest that the H_{190} peak is related to the C_i–O_i complex in irradiated $Si_{1-x}Ge_x$ samples.

Arrhenius plots of T^2-corrected emission rates for the H_{190} trap in irradiated samples with different Ge content are shown in figure 4. The activation energies for the hole emission, ΔE_p, and pre-exponential factors, A_p, derived from the plots are presented in table 2. No essential changes in the A_p values are observed. The observed changes in emission rates are related mainly to the changes in ΔE_p. Direct measurements of the hole capture were carried out for the H_{190} trap in the irradiated $Si_{1-x}Ge_x$ samples. No significant change in the σ_p values with the change in Ge content was found. The hole capture cross section for the donor level of the C_i–O_i complex has a very weak temperature dependence in $Si_{1-x}Ge_x$ as well as in

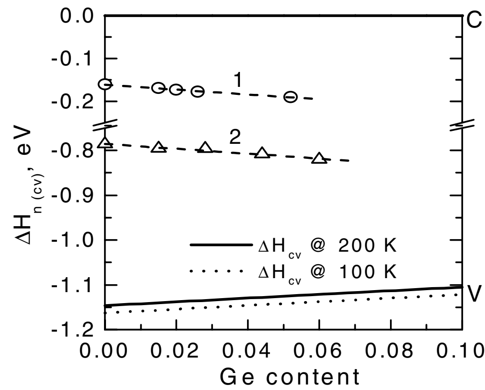

Figure 5. Enthalpies of electron ionization relative to the conduction band edge for (1) the acceptor level of the V–O centre and (2) the donor level of the C_i–O_i pair with their linear approximations (dashed lines) and enthalpy of the band gap of SiGe alloys at 100 and 200 K versus Ge content. The band gap changes were calculated on the basis of results presented in [26, 27].

Ge-free crystals [23]. Consequently, the measured values of ΔE_p for the C_i–O_i-related donor level should coincide with the values of enthalpy of the defect ionization, ΔH_p. So, the hole ionization enthalpy for the donor level of the C_i–O_i centre decreases in $Si_{1-x}Ge_x$ alloys with the increase in Ge content. There is no significant composition-related change in ionization entropy of the C_i–O_i pair in $Si_{1-x}Ge_x$ samples with $x < 6$ at.%, since the A_p and σ_p are practically the same in the samples studied.

4. Discussion and conclusions

Figure 5 shows the dependence of the ionization enthalpy of the V–O-related acceptor level on the Ge content in SiGe alloys. Composition-related changes of the band gap enthalpy, which were calculated according to results presented in [26, 27], are also shown. In agreement with recent publications [28, 29], it was assumed that the reduction of the band gap is associated with the valence band gap shift and the band gap enthalpy $\Delta H_{cv}(x, T)$ is given by [26, 27]

$$\Delta H_{cv}(x, T) = 1.17 + \alpha\beta T^2(\beta + T)^2 - 0.43x + 0.206x^2 \text{ (eV)}.$$

The observed change of ΔH_n with the change in Ge content can be approximated with a linear dependence. The rate of the ΔH_n change is found to be $d(\Delta H_n)/dx \approx 0.56$ eV. The energy level position with respect to the conduction band edge corresponds to the free energy of ionization of a defect, $\Delta G_n = \Delta H_n - T\Delta S_n$. The ΔS_n value for the V–O centre was estimated to be $-(1.2 \pm 0.4) \times k$ in Si crystals as well as in $Si_{1-x}Ge_x$ alloys with $x \leqslant 0.055$. So, at 100 K, the ΔG_n value for the V–O complex can be easily calculated as $\Delta G_n \approx \Delta H_n + 0.01$ eV. It is clear from the plot in figure 5 that the energy level of the V–O complex is not pinned to the conduction band edge or to the valence band edge. The single acceptor level of the V–O complex in Ge crystals is located in the lower part of the gap, $E(-/0) \approx E_v + 0.27$ eV [9], and the observed shift of the V–O single acceptor level in $Si_{1-x}Ge_x$ with the increase of the Ge content is consistent with this value.

The enthalpy of the hole ionization for the single donor level of the C_i–O_i centre relative to the valence band edge, ΔH_p, was found to decrease with a rate $d(\Delta H_p)/dx = -0.96$ eV with increasing Ge content. We have converted the hole ionization enthalpy to ΔH_n, the electron ionization enthalpy relative to the conduction band edge, by using the simple conservation law

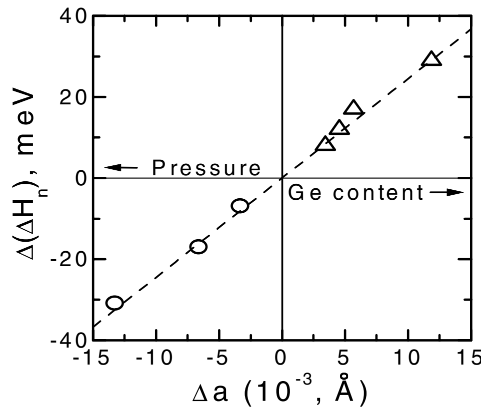

Figure 6. Changes in enthalpy of the V–O complex ionization versus changes in the lattice parameter, Δa, induced either by the application of hydrostatic pressure or by Ge doping. Δa was calculated on the basis of experimental results presented in [30, 31]. Changes in ΔH_n upon application of hydrostatic pressure were calculated on the basis of results presented in [15].

$\Delta H_p + \Delta H_n = \Delta H_{cv}$. A dependence of ΔH_n for the donor level of the C_i–O_i pair is shown in figure 5. The rate of the ΔH_n movement upon the changes in Ge content was calculated as $d(\Delta H_n)/dx = 0.55$ eV. The value obtained is very close to that for the acceptor level of the V–O complex. The C_i–O_i-related donor level is not pinned to the conduction band edge or to the valence band edge. Unfortunately, there is no information available in the literature on the electronic properties of the C_i–O_i complex in pure Ge.

The absence of pinning of the acceptor level of the A centre to the band edges was observed when the gap shrinkage of Si was induced by the application of hydrostatic pressure [15]. It should be noted, however, that while the band gap is reduced both with the increase of hydrostatic pressure and with the increase of the Ge content, the V–O-related level moved closer to the conduction band with the increase of pressure [15], i.e., in the opposite sense compared to the observed shift in SiGe alloys. Comparing the changes in enthalpy of the A centre ionization in $Si_{1-x}Ge_x$ crystals and in Si crystals upon the application of hydrostatic pressure with the changes in semiconductor parameters there is a correlation between ΔH_n for the V–O complex and the crystal lattice parameter (or the Si–Si bond length). The lattice parameter is known to decrease upon the application of hydrostatic pressure and to increase with the increase of the Ge content in SiGe alloys [30, 31]; the observed changes in enthalpy of the A centre ionization correspond with the changes in the lattice parameter (figure 6).

In summary, it has been found that electron ionization enthalpies with respect to the conduction band edge for the acceptor level of the V–O centre and for the donor level of the C_i–O_i increase with the same rate in $Si_{1-x}Ge_x$ alloys with the increase in Ge content. Neither of the energy levels are pinned to the conduction band edge or to the valence band edge. It is argued that the value of the enthalpy of the V–O ionization is very sensitive to the lattice parameter or to the Si–Si bond length: the larger this parameter the bigger the enthalpy of the ionization. Electronic structures of the V–O and C_i–O_i complexes in Si crystals are rather different [1–5]. It is not clear at the moment whether the observed similarity in $d(\Delta H_n)/dx$ values for the V–O and C_i–O_i centres is an occasional coincidence or if it reflects a general trend in composition-related changes of electronic properties of deep level defects in SiGe alloys. Similar $d(\Delta H_n)/dx$ values have been observed for a number of other deep level centres (C_i, C_i–C_s, Pt, Au, etc) in $Si_{1-x}Ge_x$ alloys [28, 32, 33].

Acknowledgments

The Engineering and Physical Sciences Research Council (EPSRC), UK, and INTAS (grant No 01-0468) are thanked for their financial support.

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