Thermal donor and antimony energy levels in relaxed $Si_{1-x}Ge_x$ layers

E. V. Monakhov, A. Yu. Kuznetsov, and B. G. Svensson
Royal Institute of Technology, Solid State Electronics, S-16440 Kista-Stockholm, Sweden

A. Nylandsted Larsen
Institute of Physics and Astronomy, Aarhus University, DK-8000 Aarhus, Denmark

(Received 23 August 1999)

Shallow energy levels in molecular-beam epitaxially grown relaxed $Si_{1-x}Ge_x$ layers with $x=0.05$ and 0.1 have been investigated by admittance spectroscopy and thermally stimulated capacitance. The shallow levels observed in as-grown layers have been identified as related to Sb and thermal donors (TD's). The Sb related donor level has an activation energy of 33 meV and 32 meV for the $Si_{1-x}Ge_x$ layers with $x=0.05$ and 0.1, respectively. For $x=0.1$, the TD's have a concentration of $\sim 5\times 10^{14}\,cm^{-3}$ and the level exhibits a gradual shift in energy position from 32 to 28 meV below the conduction-band edge during annealing at 470 °C for 36 h but no significant change in intensity occurs. The TD's appear to be single donors and no generation of the thermal double donors during the annealing at 470 °C for 36 h has been observed.

During recent years a series of investigations of shallow levels in $Si_{1-x}Ge_x$ have been performed. It was found that the ionization energies of the shallow group-V donors *P*,[1] and group-III acceptors *B*,[2] decrease with increasing Ge content, in qualitative accordance with the effective-mass theory (EMT).[3] Although one can expect other shallow donors and acceptors to follow the same trend, the experimental confirmation is still to be obtained. This holds also for oxygen-related thermal donors (TD's).

Several groups of the thermal donors originating from the oxygen clustering can be distinguished in silicon by the position of their levels in the band gap: (i) thermal double donors (TDD's) (see Ref. 4 and references therein), (ii) shallow thermal donors (STD's),[5] and (iii) ultrashallow thermal donors (USTD's).[6] The level positions for the thermal donors can be described in terms of EMT, where a TDD is a helium-like center, with the ionization energies ~60 and ~150 meV,[4] and an STD and a USTD are hydrogen-like ones, with the ionization energies ~37 meV (Ref. 5) and ~25–30 meV,[6,7] respectively. All these centers are normally formed in the temperature range of 400–550 °C. A fundamental feature of these TD's is that their ionization energies decrease gradually during heat treatment, which is normally attributed to an increase in the number of oxygen atoms clustering around the electrically active core structure of the TD's.

At higher temperatures (>600 °C) some of TD's annihilate and so-called new thermal donors (ND's) are generated. ND's are known to be of different natures; it has been reported that ND's can be double donors, single donors,[8,9] can have a band of levels,[10,11] or can be deep donors.[12] It is not quite clear whether all the ND's, formed at higher temperatures, are inherently new defects, or a redistribution of oxygen from unstable TD's that gives rise to a number of more stable donors, which may have negligible concentration at low temperatures.

The investigations of TD's in $Si_{1-x}Ge_x$ would not only give information on how different TD's obey the prediction of EMT in an alloy but also reveal the kinetics of the TD's formation and annihilation as a function of the composition. A control of the generation of TD's may have a crucial impact on the performance of $Si_{1-x}Ge_x$ based devices. However, up to now the formation of TD's in Czochralski-grown $Si_{1-x}Ge_x$ alloys was observed only for a Ge content of $\leqslant 1.5\%$.[13]

In this contribution we report on TD's and antimony shallow levels in molecular-beam epitaxially (MBE) grown relaxed $Si_{1-x}Ge_x$ layers with $x=0.05$ and 0.1 observed by admittance spectroscopy (ADSPEC) and thermally stimulated capacitance (TSCAP).

The relaxed $Si_{1-x}Ge_x$ layers with $x=0.05$ and 0.1 were grown by MBE on (100) Si substrates using the compositional grading technique. With this technique, fully relaxed layers with threading dislocation densities of less than $5\times 10^5\,cm^{-2}$ are routinely obtained.[14] The Ge content in the buffer layer was linearly graded from 0% to a required content with a grading rate of 10%/μm. The 4-μm-thick top layer of constant Ge content, in which the measurements were performed, was uniformly Sb doped to $\sim 5\times 10^{15}\,cm^{-3}$. The growth temperature and the deposition rate were 800 °C and 5 Å/s for both the graded buffer layer and the top uniform layer. High-resolution x-ray-diffraction measurements demonstrated complete relaxation of the top layer within the experimental accuracy. Investigations by secondary ion mass spectrometry revealed an oxygen content of $<5\times 10^{16}\,cm^{-3}$ and a relatively high carbon content of $\sim 10^{18}\,cm^{-3}$. Schottky diodes made by Au deposition were used in the experiment. The samples were investigated by ADSPEC and TSCAP from 15 K to room temperature at a reverse bias of 5 V and frequencies from 1 kHz to 1 MHz.

The ADSPEC and TSCAP spectra of the as-grown $Si_{1-x}Ge_x$ samples with $x=0.05$ and 0.1 are shown in Fig. 1. At least two shallow levels labeled as $L1$ and $L2$ are detected for both compositions. As seen in Fig. 1(a), the major peak ($L1$) in the ADSPEC spectra for $x=0.1$ is located at a lower temperature than that for $x=0.05$. The same is observed in the TSCAP spectra; the drop of the capacitance ($L1$) for $x=0.1$ occurs at lower temperatures than that for $x=0.05$. The position of another, minor shallow level ($L2$)

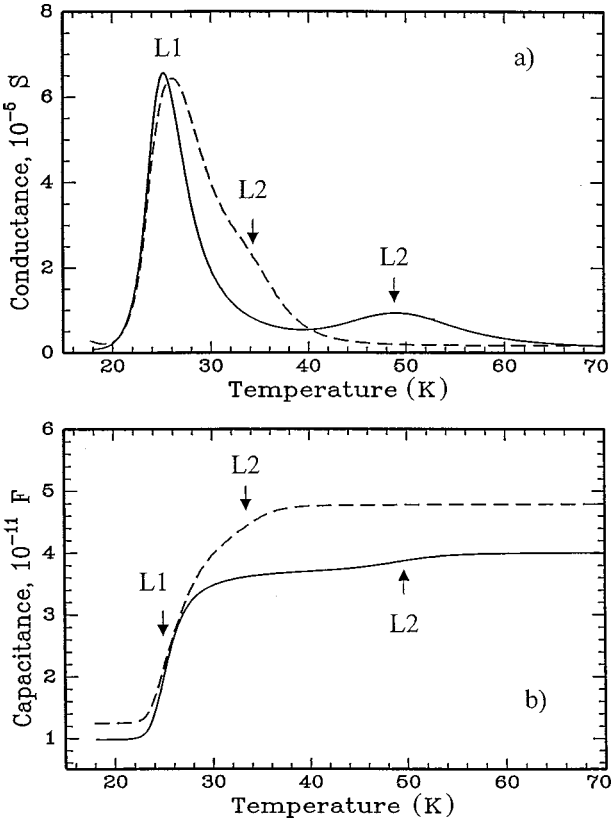

FIG. 1. ADSPEC (a) and TSCAP (b) spectra of the relaxed $Si_{1-x}Ge_x$ layers with $x=0.05$ (dashed curve) and 0.1 (solid curve).

is also different in the two samples. In the sample with $x=0.05$, $L1$ and $L2$ overlap strongly and are almost not resolvable. Because of the higher Ge content and the fact that $L1$ and $L2$ do not overlap, the sample with $x=0.1$ has been chosen for further annealing studies.

The evolution of the shallow levels in the sample with $x=0.1$ after annealing at 470 °C for different durations in an O_2 atmosphere is demonstrated in Fig. 2 (only ADSPEC

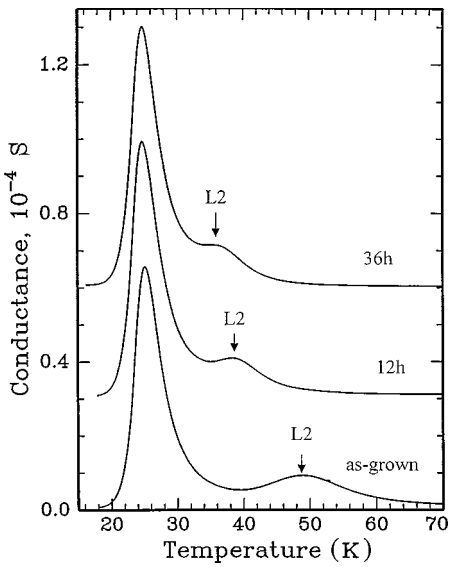

FIG. 2. ADSPEC spectra of the relaxed $Si_{1-x}Ge_x$ layers with $x=0.1$ annealed at 470 °C for different times.

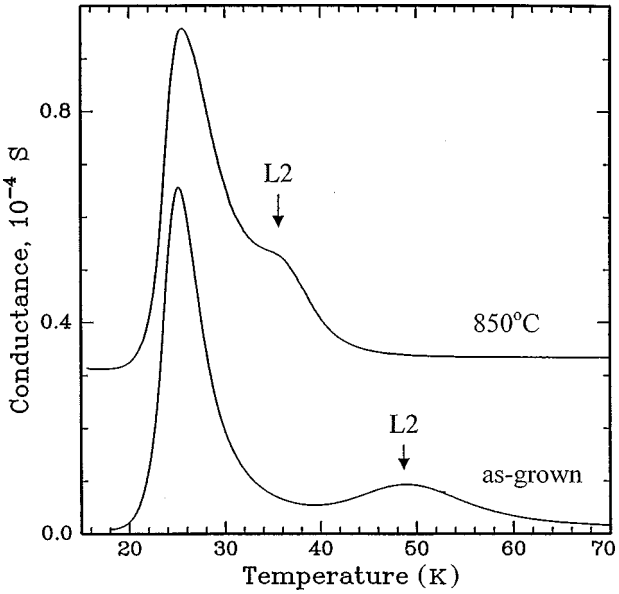

FIG. 3. ADSPEC spectra of the relaxed $Si_{1-x}Ge_x$ layers with $x=0.1$ before and after annealing at 850 °C for 14 h.

spectra are shown). It is found that the major level $L1$ in the ADSPEC and TSCAP spectra is stable for annealing times up to 36 h. In contrast, the minor level $L2$ in the ADSPEC and TSCAP spectra shifts towards lower temperatures with increasing annealing time. Despite the change in position, however, the intensity of $L2$ remains almost constant. No other donor levels have been observed to appear after the annealing at 470 °C.

The stability of the observed levels has been investigated by a high-temperature annealing at 850 °C in vacuum ($\sim 10^{-8}$ Torr) for 14 h. As shown in Fig. 3, this results in a shift of $L2$ to a lower temperature but no significant change in the intensity is observed. No effect of the high-temperature annealing on $L1$ is detected.

Arrhenius plots for $L1$ in the samples with $x=0.05$ and 0.1 and for $L2$ in the sample with $x=0.1$ deduced from the TSCAP measurements are shown in Fig. 4. The level $L1$, which is stable during the annealing, is assigned to the Sb donor, while $L2$ is identified as a TD related level. The statistical error for the activation energies presented in Fig. 4 has been estimated to be 0.5 meV.

According to EMT, the activation energy of the Sb level in $Si_{1-x}Ge_x$ must decrease with increasing Ge content. In the present investigations the activation energy of Sb in $Si_{1-x}Ge_x$ with $x=0.05$ and 0.1 is found to be 33 and 32 meV, respectively (Fig. 4). It should be mentioned that the values of the activation energies have been deduced under the assumption that the electron capture cross sections are temperature independent.

Table I contains the activation energies and the apparent capture cross sections of the observed TD's ($L2$) as determined from the TSCAP spectra for $x=0.1$ before and after annealing at 470 °C for different durations. The activation energy decreases gradually with annealing time.

The concentration of TD's in the layers can be estimated by the drop in the capacitance in the TSCAP spectra and by the peak intensity in the ADSPEC spectra (Fig. 1). Taking into account that the concentration of Sb is ~ 5

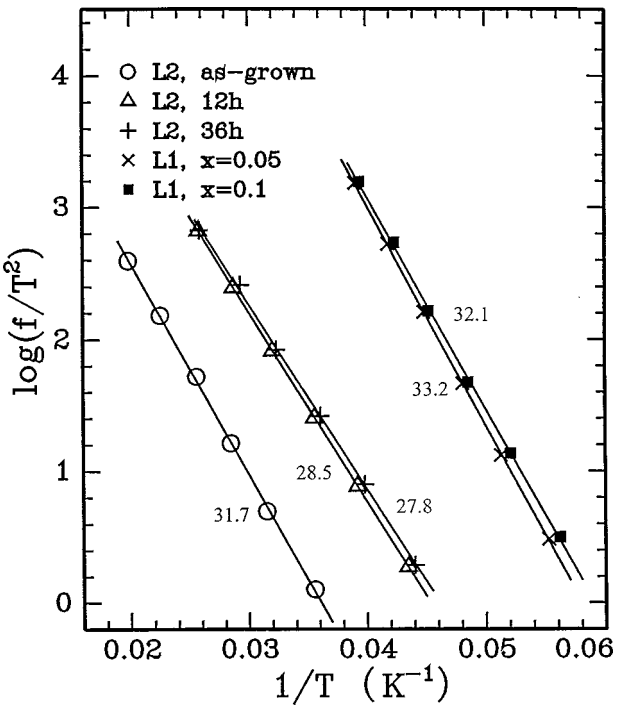

FIG. 4. Arrhenius plots for the level $L1$ in the samples with $x=0.05$ and 0.1 and for the level $L2$ in the sample with $x=0.1$. The plots were deduced from the TSCAP measurements.

$\times 10^{15}\,\mathrm{cm}^{-3}$, one can estimate the TD's concentration as $\sim 5\times 10^{14}\,\mathrm{cm}^{-3}$.

In the present investigation, there is no conclusive indication whether $L2$ is a double donor in a neutral or singly ionized state, or a single donor. However, it is established that the ionization energy of the neutral TD's in Si can vary in a relatively narrow range from 50 meV to 69 meV and that of the singly ionized from 114 meV to 156 meV.[4] On the other hand, the activation energy of the family of STD's was found to change from 37.4 meV to 34.7 meV following a dependence on the number of oxygen atoms similar to that for TDD's.[5] Theoretically, it has been shown recently that at least two families of oxygen related STD's can exist: (a) with a nitrogen atom in the core and (b) with a carbon-hydrogen complex in the core.[15,16] Because of the facts that (i) the activation energy of the TD's level (Table I) is close to that of STD's in Si, (ii) the level shifts to a shallower energy position during the heat treatment, and (iii) no other levels of similar intensity and annealing behavior, which could indicate another charge state, have been observed, it is very tempting to identify the observed TD's in the carbon-rich ($\sim 10^{18}\,\mathrm{cm}^{-3}$) $Si_{1-x}Ge_x$ layers as STD's with a carbon-based core.

TABLE I. The activation energy and the apparent capture cross section of $L2$ in $Si_{0.9}Ge_{0.1}$ as determined by TSCAP after annealing at 470 °C.

Annealing time (h)	E_1 (meV)	Cross section (cm^2)
0	31.7	5×10^{-21}
12	28.5	3×10^{-20}
36	27.8	3×10^{-20}

On the other hand, since the formation of the observed TD's occurs during the layer growth at 800 °C, $L2$ can also be attributed to ND's. As mentioned previously, ND's can have different structure, composition, and electrical properties. Because of the relatively low oxygen content in the layers ($<5\times 10^{16}\,\mathrm{cm}^{-3}$) and the evolution of the level position with time at 470 °C, the observed TD's are unlikely to originate from silicon or germanium oxide precipitates. Here it should be pointed out that hydrogen-like STD's with the activation energy in the range of 28–34 eV have been observed in carbon-rich silicon, which remain stable at temperatures from 400 °C to 800 °C.[17,18] Thus, one can again suggest that the TD's observed in the present investigations are the STD's with a carbon-based core stable up to 850 °C and with a varying number of oxygen atoms around the core structure.

In conclusion, epitaxial relaxed $Si_{1-x}Ge_x$ layers with $x=0.05$ and 0.1 grown at 800 °C by MBE have been investigated by ADSPEC and TSCAP. Sb related donor levels with activation energies of 33 meV and 32 meV for $x=0.05$ and 0.1, respectively, have been observed. For both of the compositions, other shallow donors with a concentration of about $5\times 10^{14}\,\mathrm{cm}^{-3}$ have been detected in the as-grown films. For $x=0.1$, the activation energy of these donors exhibits a gradual shift from 32 to 28 meV during annealing at 470 °C for 36 h but their concentration stays essentially constant. The shallow donors remain stable up to at least 850 °C and have been tentatively identified as carbon-oxygen related thermal donors. Any formation of thermal double donors during heat treatment at 470 °C for 36 h has not been observed.

Partial financial support was received from the Swedish Foundation for Strategic Research (SSF). One of us (E.M.) would like to thank the Wenner-Gren Center for their financial support. We are grateful to D. Åberg for his help at early stages of the experiment.

[1] R. Krüssmann, H. Vollmer, and R. Labusch, Phys. Status Solidi B **118**, 275 (1983).
[2] M. Franz, K. Pressel, and P. Gaworzewski, J. Appl. Phys. **84**, 709 (1998).
[3] R. A. Faulkner, Phys. Rev. **184**, 713 (1969).
[4] P. Wagner and J. Hage, Appl. Phys. A: Solids Surf. **A49**, 123 (1989).
[5] J. A. Griffin, H. Navarro, J. Weber, L. Genzel, J. T. Borenstein, J. W. Corbett, and L. C. Snyder, J. Phys. C **19**, L579 (1986).
[6] A. Hara, Jpn. J. Appl. Phys., Part 1 **34**, 3418 (1995).
[7] D. Åberg, M. K. Linnarson, B. G. Svensson, T. Hallberg, and J. L. Lindström, J. Appl. Phys. **85**, 8054 (1999).
[8] B. A. Andreev, V. G. Golubev, V. V. Emtsev, G. I. Kropotov, G. A. Oganesyan, and K. Schmalz, Semiconductors **27**, 315 (1993).
[9] B. A. Andreev, V. G. Golubev, V. V. Emtsev, G. I. Kropotov, G. A. Oganesyan, and K. Schmalz, Pis'ma. Zh. Eksp. Teor. Fiz. **55**,

52 (1992) [JETP Lett. **55**, 53 (1992)].
[10] K. Hölzein, G. Pensl, and M. Schulz, Appl. Phys. A: Solids Surf. **A34**, 155 (1984).
[11] K. Hölzein, G. Pensl, M. Schulz, and N. M. Johnson, Appl. Phys. Lett. **48**, 916 (1986).
[12] V. V. Emtsev, G. A. Oganesyan, and K. Schmalz, Appl. Phys. Lett. **68**, 2375 (1996).
[13] E. Hild, P. Gaworzewski, M. Franz, and K. Pressel, Appl. Phys. Lett. **72**, 1362 (1998).
[14] A. Nylandsted Larsen, J. L. Hansen, R. S. Jensen, S. Y. Shiryaev, P. R. Døstergaard, J. Hartung, G. Davies, F. Jensen, and J. W. Petersen, Phys. Scr. **T54**, 208 (1994).
[15] D. J. Chadi, Phys. Rev. Lett. **77**, 861 (1996).
[16] C. P. Ewels, R. Jones, S. Öberg, J. Miro, and P. Deák, Phys. Rev. Lett. **77**, 865 (1996).
[17] K. Schmalz, P. Gaworzewski, R. Winkler, and W. Skorupa, Phys. Status Solidi A **127**, K39 (1991).
[18] V. M. Babich, N. P. Baran, A. A. Bugai, V. I. Kiritsa, and V. M. Maksimenko, Semiconductors **30**, 417 (1996).