Determination of the valence band offset of $Si/Si_{0.7}Ge_{0.3}/Si$ quantum wells using deep level transient spectroscopy

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Deep level transient spectroscopy (DLTS) was performed on *p*-isotype Si/SiGe/Si Schottky barrier diodes in order to obtain the valence band offset between Si and SiGe. A single strained $Si_{0.7}Ge_{0.3}$ layer was placed in such a depth in Si so as to be able to fill and empty the quantized SiGe well during the transient capacitance procedure. Broad capacitance transient peaks were obtained and interpreted as being due to the capture of holes by the quantum well. The broadness of the peaks was explained by thickness variations of the SiGe layer. From the dependence of the high temperature side of the DLTS peak on the rate window a valence band offset of 220±20 meV was evaluated.

I. INTRODUCTION

The conduction- and valence-band offsets between Si and $Si_{1-x}Ge_x$ need to be known accurately in order to design strained layer devices. Common techniques for measuring conduction- or valence-band discontinuities are, for instance, the capacitance-voltage (C-V) profiling across a heterojunction[1] and the measurement of the temperature dependence of the collector current of a SiGe/Si-heterobipolar transistor.[2] Another technique, which is standard for identifying deep traps and which in recent years was successfully applied to quantum well (QW) heterostructures in III-V materials, is the deep level transient spectroscopy (DLTS). Single quantum wells (SQW) can trap carriers, as do deep traps, and therefore can be characterized by DLTS, as demonstrated by several authors.[3–7] In particular, band offsets can be determined.[3,5,7]

In this paper we present DLTS measurements performed on Si/SiGe/Si SQW structures with QWs of 2.5–4 nm nominal thickness. The energy gap difference between unstrained Si and strained SiGe was predicted to lie mainly in the valence band.[8] For this reason we have investigated *p*-type SQW structures epitaxially grown on a p^+ substrate.

II. EXPERIMENT

The samples were prepared by selective epitaxy using low pressure chemical vapor deposition (LPCVD). The epitaxy was carried out at 700 °C and 0.12 mbar on (100) Si substrates (boron, $\sim 10^{19}$ cm^{-3}). The source gases were $SiCl_2H_2$ and GeH_4 (10% in He) and doping gas was B_2H_6 diluted in H_2. The growth sequence was:

(1) a highly boron doped layer ($\sim 5\times 10^{19}$ cm^{-3}) 0.2 μm thick,
(2) 1 μm Si lowly boron doped,
(3) a very thin p-$Si_{0.70}Ge_{0.3}$ layer as QW, and
(4) a *p*-Si cap layer.

Doping level and thicknesses are given in Table I for one test sample and two SQW structures. The doping profile was obtained by electrochemical C-V profiling. Figure 1 shows the doping profile for sample 251 (see also Table I) with a QW with 3.5 nm nominal thickness. The thickness of the cap layer and the depth of the SiGe layer were obtained by Rutherford backscattering (RBS). For measuring the thickness of the SiGe layer, the cap layer was chemically thinned and then RBS was performed under 81° incidence. No dislocations were detected by photoluminescence,[9] however islands were present in the SiGe layer, as will be discussed below.

For the DLTS measurement SQW structures were grown selectively into holes etched in SiO_2 (area 0.04, 0.25, and 1 mm^2). The Schottky contact was formed by evaporating Al. Just prior to Al evaporation, the samples were dipped for 30 s in diluted HF and rinsed in deionized water. For the back ohmic contact a Ga-In alloy was used. The insert in Fig. 1 shows a schematic of the diodes used for DLTS. The diodes measured between the Al contact and the substrate showed good diode characteristics with the current scaling with diode area. The barrier height evaluated from the zero voltage intercept was 0.67 eV.

From electrochemical C-V profiling (Fig. 1) and C-V measurements on the diodes it results that the QW lies near the edge of the zero voltage depletion layer of the Schottky barrier. By applying a reverse voltage the depletion layer extends over the QW, and so the QW can be filled and emptied during the DLTS procedure. The DLTS was carried out with a variable temperature cryostat and a double boxcar system. Reverse voltages up to -5 V could be applied to the 1.3 μm thick samples before breakdown occurred. The filling pulse width was in the range 0.1 to 10 ms.

III. THEORY

For the DLTS measurement the diode is in the steady state reversely biased with the QW within the depletion region [Fig. 2(a)]. The DLTS measurement now consists of a sequence of two steps: a so called filling pulse is applied, which makes the diode less reverse or even forward biased. During this pulse holes are injected from the bulk towards the contact and are trapped by the well, if the quantized levels are deep enough. This is illustrated in Fig. 2(b) for the case that the filling voltage exceeds the reverse voltage. After the pulse is over [Fig. 2(c)], the diode is again reversely biased, but the QW is no more in equilib-

TABLE I. Data for pSi/pSiGe/pSi-SQW samples.[a]

Sample	Cap layer (d/nm)	SQW (d/nm)	SQW x	Si buffer (d/nm)	Acceptor conc./ cm^{-3}	ΔE_v/ meV
249	300	0	0	1000	5×10^{16}	0
251	320	3.5	0.3	1000	$(1–5)\times10^{16}$	220
252	580	2.7	0.3	1000	$(2–5)\times10^{16}$	220

[a] The test sample 249 was grown under the same conditions as the SQW.

rium with the rest of the bulk because of the trapped holes. Hole emission will take place until the QW reaches the same steady state as the bulk.

In order to analyze the QW-DLTS measurements it is necessary to calculate the occupation of the hole levels in the QW and the time-dependent emission of holes. This will allow the evaluation of the temporal variation of the capacitance. The following analysis is based on a model of Letartre *et al.*[7] The statistics of the holes in a 2D system gives for the occupation of i quantum levels the expression

$$p_w=\frac{m^*_{\mathrm{SiGe}}}{\pi\hbar^2}\,kT\,\sum_i \ln\left[1+\exp\left(-\frac{E_{FW}-E_i}{kT}\right)\right], \tag{1}$$

where m^*_{SiGe} is the effective hole mass for a given Ge concentration and E_{FW} is the quasi-Fermi level for the QW (see Fig. 2). The energy levels E_i in the SiGe well were calculated using the one-particle Schrödinger equation. As the SiGe layer is under compressive strain the degeneracy at the Γ point is lifted, the light hole band being shifted to lower energy.[10] This shift is $\sim$50 meV for 20% Ge. In principle, the energy levels and their occupation should be calculated for both heavy and light holes, using corresponding effective masses and valence band offsets. However, the following evaluations will show that only the highest heavy hole level (nearest to the bottom of the well) is involved in the DLTS process.

During the filling pulse the QW is supposed to reach a maximum occupation, which is for instance for an acceptor concentration $N_a\sim10^{16}\,\mathrm{cm}^{-3}$, $m^*_{\mathrm{SiGe}}\sim0.25m_0$, $T=100$ K, and a valence band offset $\Delta E_v\sim200$ meV: $p_w^0\sim2\times10^{11}$ cm^{-2}. However, for 10 meV between the first two hole levels E_1 and E_2 the number of holes which can be accommodated on E_1 is higher, i.e., $1\times10^{12}\,\mathrm{cm}^{-2}$. Therefore, E_1 is only partly occupied, all other levels are empty and can be neglected, including the light hole levels (which lie at lower energy due to the compressive strain shift).

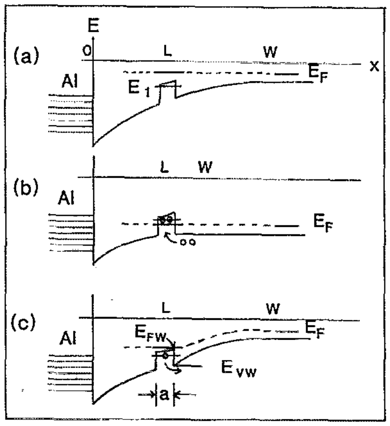

FIG. 2. Qualitative band scheme of the Schottky barrier on a p-isotype heterostructure with a SQW in the depletion region. (a) Under reverse bias V_{rev} in steady state the well is empty; (b) under bias $V_{\mathrm{rev}}-V_{\mathrm{fill}}$ during the filling pulse the well has its maximum occupation; (c) under reverse bias V_{rev} during the emission phase.

After the filling pulse is over, holes will be thermionically emitted from the SiGe well into the Si barrier and so the occupation p_w will decrease in time. Assuming for the barrier of the holes $E_{FW}-E_{VW}\gg kT$ one gets

$$\frac{dp_w}{dt}=-\frac{4\pi m^*_{\mathrm{Si}}}{h^3}\,(kT)^2\exp\left[-\frac{E_{FW}(p_w)-E_{VW}}{kT}\right], \tag{2}$$

where E_{VW} is the "top" of the quantum well barrier (Fig. 2). The position of the quasi-Fermi level E_{FW} changes with p_w, and so from Eqs. (1) and (2) $p_w(t)$ can be calculated.

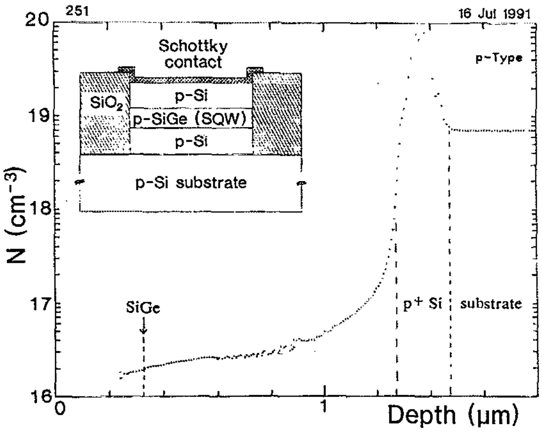

FIG. 1. Electrochemical C-V profile for a p-type sample with a SiGe QW with nominal thickness of 3.5 nm (the position of the QW is marked by a dashed line). In the insert the schematics of the pSi/pSiGe/pSi diode is shown.

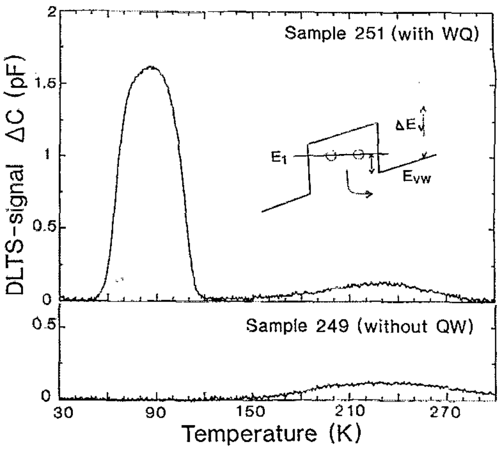

FIG. 3. DLTS spectra of a sample without QW (bottom) and a sample with a QW (top: sample of Fig. 1); $V_{\mathrm{rev}}=-1$ V, rate window=200/s, $V_{\mathrm{fill}}=0.2$ V, and $t_p=10$ ms.

Due to the high density of states of the subbands the Fermi level E_{FW} lies during the emission process several kT above E_1. Therefore, Eq. (1) simplifies to

$$p_w=\frac{m^*_{\mathrm{SiGe}}}{\pi\hbar^2}kT\exp\left(-\frac{E_{FW}-E_1}{kT}\right). \tag{3}$$

The solution of Eqs. (2) and (3) gives the time dependence of the occupation

$$p_w(t)=p_w^0\exp(-e_w t), \tag{4}$$

where e_w is the emission rate of holes. For thin wells, where the highest level E_1 dominates ($E_1-E_2\gg kT$), the emission rate is given by

$$e_w=\frac{m^*_{\mathrm{Si}}}{m^*_{\mathrm{SiGe}}}\frac{kT}{h}\exp\left(-\frac{E_1-E_{VW}}{kT}\right). \tag{5}$$

Therefore, E_1-E_{VW} is the barrier for emission of holes and can be measured by DLTS in a similar way as for deep traps, where an activation energy results. The only difference is that the preexponential factor is $\sim T$ and not $\sim T^2$. If the QW width a is known, the valence band offset can be calculated from

$$\Delta E_V=(E_1-E_{VW})+\Delta E_1+\frac{eN_a}{\epsilon}(W-L)\frac{a}{2}, \tag{6}$$

where W is the width of the depletion layer, L is the distance of the well from the surface, and ΔE_1 is the distance of the highest heavy hole level to the bottom of the well. The third term in Eq. (6) is the barrier lowering due to the finite dimension of the QW. The change of capacitance ΔC is directly related to the hole occupation $p_w(t)$. For $\Delta C/C\ll 1$ the solution of Poisson's equation leads to[5]

$$\frac{\Delta C}{C}\approx\frac{1}{2}\frac{L}{W^2}\frac{p_w}{N_a}. \tag{7}$$

IV. RESULTS AND DISCUSSION

Measured DLTS signals are shown in Fig. 3 for a sample without QW (bottom) and for a sample with a 3.5 nm QW (top). Both samples were measured under the same conditions. Both samples reveal a small and broad peak in the range 230 K, which was found to be related to deep traps in Si of a concentration of $\sim 2\times 10^{13}$ cm^{-3}. However, only the QW sample 251 reveals a strong peak at ~ 100 K. This peak was observed in all investigated SQW samples.

Now, we can compare the calculated capacitance signal $\Delta C/C$ with the measured one. This is done in Fig. 4 for two different barriers. The comparison shows, that the experimental peak is much broader than the calculated peaks. The reason for the broadness of the measured QW peak is very probably the thickness inhomogeneity of the SQW layer. In cross section transmission electron micrographs a continuous and homogeneous layer ~ 2 nm thick was seen having a sharp bottom interface, but in certain distance (~ 300 nm) islands of 5–10 nm were present. For thicker QWs the highest energy level lies closer to the bottom than for thinner ones, therefore the barrier height is higher for the islands. This means, that the *right flank of the DLTS peak is given by the islands,* while the broadening to left side is due to thinner regions of the SiGe layer (see Fig. 4).

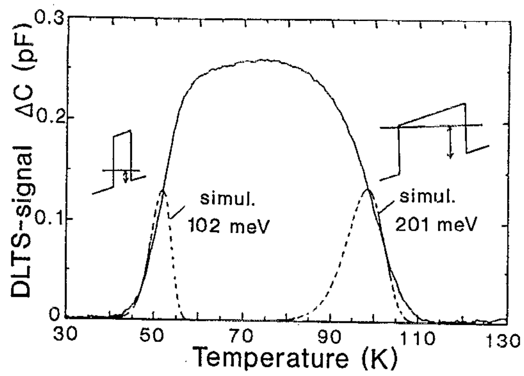

FIG. 4. QW-related DLTS peak of sample 251 compared with calculated transients for two different barriers $E_1-E_{VW}=102$ and 201 meV. The DLTS measurement was performed at: $V_{\mathrm{rev}}=-2$ V, rate window=200/s, $V_{\mathrm{fill}}=0.3$ V, $t_p=10$ ms.

The origin of the measured DLTS signals as being due to interface states can be excluded by two arguments. First, if the DLTS peaks were caused by interface states the distribution of interface states in the gap should go abruptly to zero at 0.2 eV, because of the very steep right flank of ΔC. This would be an atypical behavior of interface states, normally they have a broad energetic distribution. Second, the DLTS signal shifts strongly to lower temperature as the reverse voltage is increased, as seen in Fig. 5. This behavior shows a larger spatial extension of the potential unusual for localized states. However, a quantum well with ~ 10 nm width is expected to show a barrier lowering (Poole–Frenkel effect) with increasing field as observed.

The analysis of the DLTS signal cannot be made as usual by using the peak temperature for a given rate window because the peaks are too broad. Instead, we used the half height of the right flank and looked for its shift with the rate window. The so defined emission rate is represented in Fig. 6 for eight rate windows. One can see, that it varies exponentially with temperature exhibiting an activation energy of 200±10 meV. For a 8 nm thick QW the highest level is 14 meV above the well bottom. With a

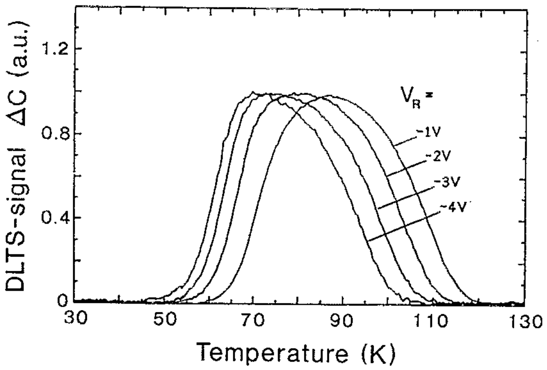

FIG. 5. DLTS signal of sample 251 for different reverse voltages; rate window 400/s, $V_{\mathrm{fill}}=0$ V, $t_p=10$ ms.

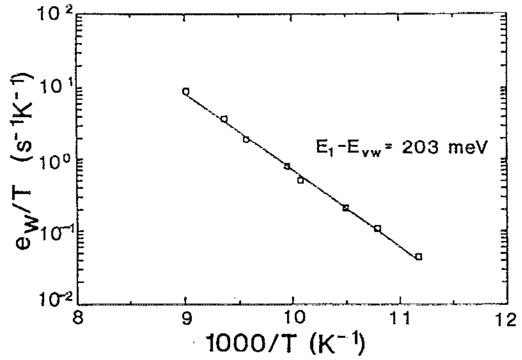

FIG. 6. Arrhenius plot of the right flank of the DLTS peak for eight different rate windows (4, 10, 20, 50, 80, 200, 400, and 1000 s^{-1}). Measurements performed at: $V_{rev} = -1$ V, $V_{fill} = 0.2$ V, $t_p = 10$ ms.

barrier lowering of 8 meV (from N_a and the depth L of the QW, see Table I) a valence band offset of 220±20 meV results, taking for m^*_{SiGe} the value $0.25m_0$.[9]

V. CONCLUSIONS

In conclusion, p-type $Si_{0.7}Ge_{0.3}$/Si SQWs of 2–4 nm average thickness were investigated by DLTS. A broad DLTS peak was obtained, which was found to be due to holes emitted from the QW. This enabled the determination of a valence band offset of 220 meV for $x = 0.3$. The form of the DLTS peak reflects the interface morphology of the QW, which in this particular case, due to the presence of islands leads to broadening of the DLTS peaks.

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