Quantum-confined direct-gap transitions in tensile-strained Ge/SiGe multiple quantum wells

Lee Carroll,^{1(a)} Florian Imbert,¹ Hans Sigg,¹ Martin Süess,² Elisabeth Müller,² Michele Virgilio,^{3,4} Giovanni Pizzi,^{3,5} Peggy Roszbach,⁶ Daniel Chrastina,⁷ and Giovanni Isella⁷

¹Laboratory for Micro- and Nanotechnology, Paul Scherrer Institut, CH-5232, Switzerland

²Electron Microscopy ETH Zurich (EMEZ), ETH-Zurich, CH-8093, Switzerland

³NEST, Istituto di Nanoscienze, CNR-Nano, I-56127 Pisa, Italy

⁴Dipartimento di Fisica "E. Fermi", Università di Pisa, I-56127 Pisa, Italy

⁵Scuola Normale Superiore, Piazza dei Cavalieri 7, I-56126 Pisa, Italy

⁶EMPA-Duebendorf, CH-8600 Dübendorf, Switzerland

⁷L-NESS, Dip. di Fisica del Politecnico di Milano, Polo di Como, via Anzani 42, I-22100 Como, Italy

(Received 14 February 2011; accepted 3 June 2011; published online 22 July 2011)

Tensile-strained Ge/Si_{1-x}Ge_x ($x=0.87$) multiple quantum wells (MQWs) on a Ge-on-Si virtual substrate are investigated with Brewster transmission and photo-reflectance, to identify quantum-confined direct-gap transitions and their light/heavy-hole splitting. Strain is deduced from optical splitting and x-ray diffraction measurements. As-prepared MQWs have an exciton at ≈ 820 meV, close to the 810 meV edge of the telecommunication C-band. The effect of rapid thermal annealing, to red-shift this feature into the C-band via increased strain, is investigated and interpreted with a tight-binding model. Annealing is observed to red-shift bulk absorption, but MQW transitions experience a net blue-shift due to interdiffusion. © 2011 American Institute of Physics. [doi:10.1063/1.3606383]

To integrate Ge/SiGe multiple quantum wells (MQWs) into a complementary metal–oxide semiconductor compatible telecom platform, tensile strain is needed to lower the direct-gap (DG) transitions in the quantum wells (QWs) towards the telecommunication windows. Of particular interest are suitably strained MQW detectors and modulators¹ where the absorption onset and sharp exciton resonance overlap with the 1.530–1.565 μm (810–792 meV) C-band window. Furthermore, optically pumped lasing has recently been reported from n-type doped, tensile strained Ge-on-Si layers.² For this bulk Ge-on-Si laser system, the tensile-strain reduces the direct-indirect band separation (between the Γ and L conduction band minima), increasing the population of electrons in the Γ -valley and promoting DG emission. While quantum-confined DG transitions,³ Stark-shifts,⁴ and transient gain⁵ have already been observed in compressively-strained Ge/SiGe MQWs, results from tensile-strained Ge/SiGe MQWs have only recently been reported. Y Chen *et al.* have shown that tensile-strained Ge/SiGe MQWs on a Ge-on-Si virtual substrate (VS) can be prepared,⁶ but present only 100 meV-broad room-temperature (RT) photoluminescence (PL) peaks as evidence of quantum-confined DG transitions. In this letter, we use transmission and photo-reflectance spectroscopy to provide definitive evidence of quantum-confined DG transitions in tensile-strained Ge/SiGe MQWs. Increased sample strain after post-growth rapid thermal annealing (RTA) is investigated, and the effect on the DG transitions measured and modelled using a tight-binding (TB) approach.⁷

The 10-period Ge/SiGe MQW heterostructures and 2 μm Ge-on-Si VS were grown using low-energy plasma-enhanced chemical vapor deposition (LEPECVD).⁸ The Ge-on-Si VS was grown at 500 °C on a Boron-doped (1–10 Ω cm) Si-sub-

strate, at a rate of 4.2 nm s⁻¹, and then annealed 6 times between 600 °C and 820 °C with a ramp rate of 2 °C s⁻¹. Photodiodes fabricated from similar material demonstrate good responsivity and low dark current, indicating a low threading dislocation density and background doping⁹ (estimated $< 1 \times 10^{17}$ cm⁻³). The MQW structures were grown on the VS at 520 °C with a nominal rate of 0.26 and 0.29 nm s⁻¹ for the QWs and barriers, respectively. X-ray diffraction (XRD) measurements give nominal barrier and QW widths of 8.8 nm and 17.6 nm, respectively. The barrier composition is determined as Si_{1-x}Ge_x ($x=0.87$), and the QWs pure Ge ($>99\%$). Secondary ion mass spectroscopy was used to verify that the Ge-layer in the VS was Si-free to $< 0.1\%$. Brewster transmission and photo-reflection measurements were carried-out on 7 mm $\times$ 7 mm “chips” diced from the sample wafer, and chemical-mechanically polished on the back face. A series of post-growth RTA samples, for enhanced tensile-strain, was prepared between 650 °C and 850 °C in an inert-atmosphere oven. The sample chips were held at their maximum temperature for 30 s (5 s and 1 s for “flash-annealed” samples) and cooled at 28 °C/s (from 850–600 °C), limited by the thermal inertia of the oven. During annealing, the chips were protected with a 200 nm PECVD silicon oxide layer.

Figure 1(a) shows the transmission-spectrum (and first-derivative) of the as-prepared MQW sample, along with the first-derivative spectra of a series 30 s RTA samples. The sharp features below 800 meV are due to the light-hole to the conduction band Γ point (LH-c Γ), and heavy-hole to conduction band Γ point (HH-c Γ), absorption edges of the bulk Ge-on-Si VS. For moderate in-plane strain, this VS LH-HH splitting (Δ) is linearly related to the biaxial tensile-strain ($\epsilon_{\parallel}$) by $\Delta = (6700 \pm 50) \text{ meV} \times \epsilon_{\parallel}$.¹⁰ Without post-growth RTA, the VS biaxial tensile-strain (as deduced from transmission) is 0.17% from the sample growth conditions. This was independently verified using XRD rocking-curve

^{a)}Electronic mail: lee.b.carroll@gmail.com.

FIG. 1. (Color online) (a) Brewster-geometry transmission spectrum of the as-prepared sample, and the first-derivative spectra on the RTA series. The line-shape is fitted to a qualitative model to extract the MQW1 and MQW2 transition energies. (b) PR-spectrum of the as-prepared sample, clearly resolving individual light/heavy-hole transitions in MQW1 and MQW2. The PR-spectrum is fit with a TDF model to extract the LH/HH transition energies.

measurements ($\epsilon_{II} = 0.16 \pm 0.01\%$). As they are grown coherently on the VS (verified by XRD reciprocal space map measurements) the Ge/SiGe MQWs also have this 0.17% strain. Two quantum-confined DG transitions can be resolved in the first-derivative spectra, and using the TB model they are attributed to the superposition of LH1/HH1-cΓ1 transitions, termed “MQW1”, at 824 ± 1 meV and to the superposition of LH2/HH2-cΓ2 transitions, termed “MQW2”, at 895 ± 3 meV, with a dominant contribution from the LH transitions. In fitting the line-shape of the first-derivative spectra, the under-shoot of MQW1 is reproduced by including an exciton feature (in addition to the expected 2D band-to-band transition). Our purely qualitative model uses *erf*-functions for the 2D band-to-band transitions and a Gaussian peak for the exciton feature.

Photo-reflectance (PR) spectroscopy¹¹ was performed using light from a filament lamp, transmitted through a grating spectrometer and focussed to a $750 \mu\text{m}$ spot is used as the probe, with a 50 mW, 532 nm CW laser for excitation. As shown in Figure 1(b), the PR spectrum of the as-prepared sample resolves the LH-HH splitting of the quantum-confined MQW1 and MQW2 transitions (in addition to the bulk VS splitting). After accounting for the thin-film interference of the Ge-on-Si VS, the PR spectrum can be fitted using the standard third-derivative functional form (TDF) model,¹² with exciton, 3D band-to-band, and 2D band-to-band critical points. An exciton feature is needed to properly fit the MQW1 transition. The transmission spectrum of the as-prepared sample gives the MQW1 transition at 824 ± 1 meV, and PR of the same material

resolves the HH1-cΓ1 transition at 819 ± 1 meV. This indicates that the strained Ge/SiGe MQWs have an exciton feature just 9-14 meV from the infrared telecommunication C-band (Erbium window: 810-792 meV). An exciton feature so close to the C-band is already of technological interest, because the absorption band can be fully shifted into the band using moderate Stark-effect tuning fields.¹³ The possibility of red-shifting this exciton feature further into the C-band motivated the investigation of the RTA samples.

As expected, RTA increases the strain of the MQWs - from 0.17% to 0.24%, see Figure 2(a), and red-shifts the Ge-on-Si VS absorption edges. However, both MQW1 and MQW2 transitions experience a *blue*-shift, as shown in Fig. 2(b), even for the lowest RTA of 650 °C. In the RTA samples, MQW1 and MQW2 can be resolved up to 750 °C but after 800 °C, only a single feature at ≈ 895 meV in transmission is observed. This coincides closely with the 902 meV DG of the strained $\text{Si}_{1-x}\text{Ge}_x$ ($x = 0.96$) alloy given by the stoichiometric mix of QWs and barriers. The net blue-shift of MQW1 away from the C-band is explained by annealing-induced inter-diffusion between the barriers and QWs. A numerical model is constructed, starting with the as-prepared profile (assuming sharp interfaces, periodic boundary conditions, fixed nominal barrier composition and dimensions).

For the annealed samples, alloy inter-diffusion is calculated using the temperature dependent linear diffusion-constant values extrapolated from (i) the literature,¹⁴ and (ii) from our own XRD determination. As per the XRD data, we assume coherent growth of the MQWs without relaxation of the in-plane tensile-strain. We assume a constant in-plane lattice parameter for each sample, deduced from the VS LH-HH splitting. The z-dependent lattice constant in the growth direction is evaluated by means of macroscopic elastic theory, where the Poisson ratio is calculated using (i) the deduced inter-diffusion profile, (ii) the relaxed lattice parameters and (iii) elastic constants of the SiGe, based on a linear interpolation of the pure Si and Ge values. The generated layer profiles are then used to calculate the relevant inter-band electronic states by means of a TB code, where the measured Ge concentrations and layer thicknesses are used as input parameters.⁷ In order to better reproduce the MQW electronic states throughout the whole Brillouin zone (BZ), our TB parameterization is obtained semi-empirically to reproduce the overall valence and conduction band dispersion and deformation potentials at the relevant bands edges.^{3,15,16} The calculated transition energies are given in Fig. 2(c), with both the transition energies and the general trend of a blue-shift in MQW1 and MQW2 being reproduced. The measured onset of inter-diffusion (taken as the first net blue-shift of the transitions) occurs at 650 °C, while the model based on literature values predicts 700 °C. Careful calibration of the RTA oven (melting of Al and Ge test samples) confirmed the accuracy of our temperature-readings. The stronger-than-expected diffusion of the 800 °C, 750 °C and 650 °C 30 s annealed samples was verified by XRD analysis of the first super-lattice (SL) satellite peak.¹⁷ Our SL signal reduction is found to be a factor of 5.5 times stronger than the existing values, equivalent to a 50K temperature-shift. It should be noted that reported values of the linear diffusion constant for Ge/SiGe MQWs can vary by 50 K (see Refs. 14,18). The model based on our own XRD-determined diffusion constant gives

FIG. 2. (Color online) (a) LH-HH splitting from transmission and PR data, and the corresponding biaxial strain of the VS, as a function of RTA time and temperature. (b) Transmission and PR determinations of MQW1 (LH1/HH1-c Γ 1) and MQW2 (LH2/HH2-c Γ 2) transition energies, as a function of 30 s RTA. (c) TB calculations of the LH1/HH1-c Γ 1 and LH2/HH2-c Γ 2 transitions, taking the linear diffusion-constant from (i) the literature and (ii) our own XRD determination.

improved agreement, but still predicts only a very modest red-shift of MQW1, which could easily be offset by the natural variation in QW thickness in different “chips”. In an effort to decouple the role of strain and inter-diffusion, some chips were “flash-annealed” to their maximum temperature for just 1 s or 5 s. However, as shown in Fig. 2(a), flash-annealing to below 800 °C does not increase the tensile strain, while annealing for even 1 s above 800 °C removes all traces of MQW features from the PR spectra.

The TB calculations in Fig. 2(c) only include the difference between energy states at the Γ -point of the BZ for MQW1, or the BZ boundary along the growth direction for MQW2. Accounting for the k_z band dispersion could bring the model and the experimental data into even better agreement. The band dispersion calculations, using our XRD-determined diffusion constant, are used to estimate the annealing-induced transition-broadening, due to joint density of states dispersion along the growth direction. This dispersion is mainly due to coupling of valence states confined in neighbouring QWs and increases for highly inter-diffused QW profiles. Assuming negligible dependence of the dipole matrix elements on k_z , the strength of the transmission features are inversely proportional to such broadening. This is clearly demonstrated in Fig. 3, where the measured MQW1

FIG. 3. (Color online) (a) Absorption strength of the MQW1 and MQW2 transitions, as determined from the transmission spectra. (b) The inverse transition broadening of the LH1/HH1-c Γ 1 and LH2/HH2-c Γ 2 transitions, as calculated from the TB model taking the linear diffusion-constant from our own XRD determination.

and MQW2 feature-strength and calculated inverse-broadening differ only by a scaling factor.

Finally, transmission electron microscopy (TEM) cross-section images of the as-prepared and 30 s 750 °C annealed samples were compared. The concentration of defects at the interface between the VS and MQWs is significantly higher for the case of the 750 °C sample. We speculate that these defects act to promote the observed inter-diffusion between the wells and barriers at relatively low temperatures.

In summary, quantum-confined DG transitions have been clearly identified in 0.17-0.24% tensile-strained Ge/SiGe MQWs. The as-prepared MQWs have an exciton feature just 9-14 meV from the C-band edge. TB calculations are used to identify the different LH/HH transitions. RTA of the samples increases their strain, red-shifting the VS absorption edges, but the quantum-confined transitions experience a net blue-shift, due to strong inter-diffusion. In future, it is hoped that LEP-ECVD growth of Ge/SiGe MQWs directly onto 850 °C pre-annealed Ge VS will offer the strain needed for LH1-c Γ 1 to enter the C-band, and bypass inter-diffusion effects entirely.

Part of this work is supported by the Swiss National Science Foundation (SNF#130181). We thank Stefan Stutz and Anja Weber for sample preparation.

- ¹Y.-H. Kuo *et al.*, *Nature (London)* **437**, 1334 (2005).
- ²J. Liu *et al.*, *Opt. Lett.*, **35**, 679 (2010).
- ³M. Virgilio *et al.*, *Phys. Rev. B* **79**, 075323 (2009).
- ⁴S. Tsujino *et al.*, *Appl. Phys. Lett.* **89**, 262119 (2006).
- ⁵C. Lange *et al.*, *Phys. Rev. B* **79**, 201306R (2009).
- ⁶Y. Chen, C. Li, H. Lai, and S. Chen, *Nanotechnology* **21**, 115207 (2010).
- ⁷G. Pizzi, M. Virgilio, and G. Grosso, *Nanotechnology* **21**, 055202 (2010).
- ⁸G. Isella *et al.*, *Solid State Electron.* **48**, 1317 (2004).
- ⁹J. Osmond *et al.*, *Appl. Phys. Lett.* **94**, 201106 (2009).
- ¹⁰Y. Ishikawa *et al.*, *J. Appl. Phys.*, **98**, 013501 (2005).
- ¹¹J. L. Shay, *Phys. Rev. B*, **2**, 803 (1970).
- ¹²H. Shen *et al.*, *Appl. Phys. Lett.* **48**, 653 (1986).
- ¹³D. J. Paul, *Phys. Rev. B* **77**, 155323 (2008).
- ¹⁴N. Ozguven and P. C. McIntyre, *Appl. Phys. Lett.*, **92**, 181907 (2008).
- ¹⁵M. Bonfanti *et al.*, *Phys. Rev. B* **78**, 041407 (2008).
- ¹⁶M. De Seta *et al.*, *Appl. Phys. Lett.* **95**, 051918 (2009).
- ¹⁷J.-M. Baribeau, *J. Vac. Sci. Technol. B* **16**, 1568 (1998).
- ¹⁸X.-C. Liu and D. R. Leadley, *J. Phys. D: Appl. Phys.* **43**, 50530 (2010).