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Thermal relaxation processes in $Si_{1-x}Ge_x/Si$ quantum wells studied by inter-subband and inter-valence band spectroscopy

B. Adoram[a], D. Krapf[a], M. Levy[b], R. Beserman[b], S. Thomas[c], K.L. Wang[c], J. Shappir[a], A. Sa'ar[a,*]

[a] *Department of Applied Physics, The Fredi and Nadine Herrmann School of Applied Science, The Hebrew University of Jerusalem, Jerusalem 91904, Israel*

[b] *Solid State Institute and Physics Department, The Technion, Haifa 32000, Israel*

[c] *Department of Electrical Engineering, University of California at Los Angeles, CA 90024, USA*

Abstract

In this paper we present a systematic experimental investigation of the optical properties associated with inter-subband and inter-valence band transitions in p-type pseudomorphic $Si_{1-x}Ge_x/Si$ multiple quantum-wells structure under high-temperature thermal treatments. The structure exhibits two types of optical absorption lines: the first obeys the inter-subband selection rules and is assigned to heavy-hole transitions while the second obeys the inter-valence band selection rules and is assigned to transitions between a heavy hole and a mixed spin split off and light-hole state. Annealing treatments reveal two kinds of thermally activated processes. The first process is assigned to strain relaxation while the second is assigned to Si and Ge inter-diffusion. Raman spectroscopy provides additional support to our interpretation of the activation processes. We propose a quantitative model, based on the Bir–Pikus deformation potential to explain the experimental results.

Keywords: Silicon–germanium quantum wells; Inter-valence band transitions; Strain relaxation; Inter-diffusion

Pseudomorphic silicon–germanium (SiGe) heterostructures grown on Silicon (Si) substrates have extensively been investigated over the recent years for silicon-based optoelectronic applications. Due to the large valance band discontinuity between Si and SiGe strained alloys, this semiconductor system is suitable for fabricating p-type quantum-well infrared photodetectors (QWIPs) that can monolitically be integrated with Si-based readout circuits [1]. However, standard Si-processing technology involves high-temperature thermal treatments that may cause a severe degradation in device's performances [2]. Therefore, it is essential to understand how thermal annealing processes [3–5] affect the optical properties associated with transitions within the valance band in SiGe/Si heterostructures.

In this work, we study the influence of thermal annealing processes on the optical transitions within the

* Corresponding author. Tel.: +972-2-6585701; fax: +972-2-5663878.

E-mail address: saar@vms.huji.ac.il (A. Sa'ar)

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valance band in p-type pseudomorphic Si/SiGe QWs. Infrared (IR) absorption spectroscopy was applied to probe various thermally activated processes and their influence on the optical properties of these heterostructures.

The sample used for our study was grown by molecular beam epitaxy (MBE) on a high resistivity (1500 Ω cm) n-type (100) Si substrate. It consists of 20 periods of SiGe/Si QWs. Each period consists of a 30 Å wide $Si_{0.77}Ge_{0.23}$ QW, boron (p-type) doped to a level of 9.6×10^{11} cm^{-2} and a 500 Å undoped Si barrier. In addition, a 300 Å wide $Si_{0.77}Ge_{0.23}$ layer and boron doped to a level of 4×10^{18} cm^{-3}, was grown on top of the QWs. The whole structure is capped with 5000 Å top and bottom Si contact layers and boron doped to a level of 10^{19} cm^{-3}. Both the contact and the wide well layers are used for detector's application to be discussed elsewhere. IR absorption measurements were recorded using a Perkin-Elmer 2000 Fourier transform infrared spectrometer (FTIR) with the sample polished to standard 45° multi-pass waveguide geometry. In this geometry, the polarization of the IR beam can continuously be changed from s- to p-polarization (i.e. polarization normal and parallel to the growth direction).

Infrared transmission spectra at various polarization angles of the as grown sample were shown elsewhere [6]. In brief, two absorption lines at 3.8 and 6.1 μm, polarized perpendicular to the growth direction, and an additional line at 10 μm, polarized parallel to the growth direction have been observed. We assign the 10 μm absorption line to the HH1 → HH2 inter-subband transition (ISBT) in the QWs, (where HH stands for heavy-hole subbands), while the 6.1 and the 3.8 μm absorption lines are assigned to the HH1 to a mixed light hole (LH) and spin-split-off (SO) state (SO+LH)1 inter-valence band transitions (IVBTs) in the semi-bulk 300 Å wide SiGe strained layer and the QWs, respectively. The origin of the SO and LH inter-mixing is the QW confinement and the strain [7,8]. The IVBT at 6.1 μm fits very well to the energy separation between the HH and SO levels in semi-bulk strained $Si_{0.77}Ge_{0.23}$.

Thermal annealing has been preformed in a Nitrogen gas ambient furnace for 1 h at temperatures between room temperature and 1060°C and the IR absorption spectra were recorded after each thermal process. At the insets of Figs. 1(a) and (b) we plot

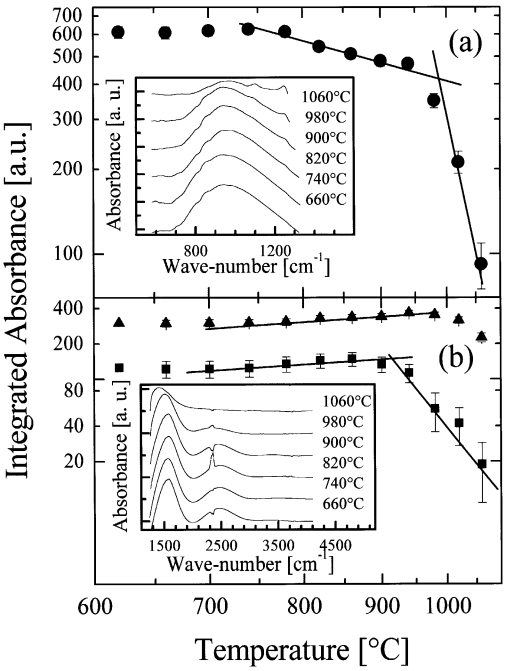

Fig. 1. (a) Arrhenius plot of the ISBT integrated absorbance (●) versus the annealing temperature. The solid lines represent the two activation processes. (b) The same for the QW IVBT (■) and the semi-bulk IVBT (▲). The insets in (a) and (b) show the ISBT and IVBT absorption spectra at various annealing temperatures respectively.

the ISBT and IVBT absorption lines at various temperatures. Let us define the integrated absorbance as the area below each absorption line. Arrhenius plots of the integrated absorbance versus the annealing temperature for the ISBT and IVBT absorption lines are shown in Figs. 1(a) and (b).

Several activation processes can be deduced from these figures. At temperatures higher than 940°C the integrated absorbance of both QW absorption lines decreases with the increasing temperature. The activation energy of both lines is approximately the same, $\Delta E_D \cong (1.9 \pm 0.2)$ eV. The semi-bulk IVBT (6.1 μm) shows a weaker decrease that begins at slightly higher temperatures. In the temperature range, 750–940°C, we observed an additional thermally activated process. Here, the QW ISBT integrated absorbance decreases with the increasing temperature with an activation energy of $\Delta E_S \cong (0.13 \pm 0.02)$ eV while the integrated absorbance of both IVBTs increases with the increasing temperature with $\Delta E_S \cong$

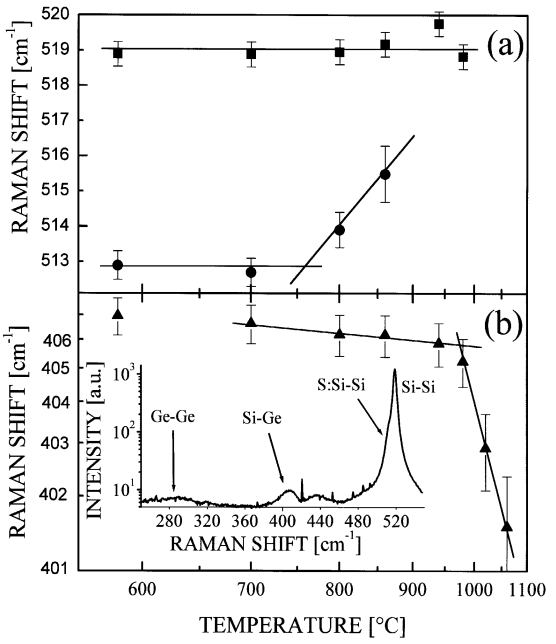

Fig. 2. (a) Raman shifts of the strained (●) and unstrained (■) Si–Si phonon lines. (b) The same for the SiGe phonon line (▲). Inset: a typical Raman spectra after annealing at 700°C.

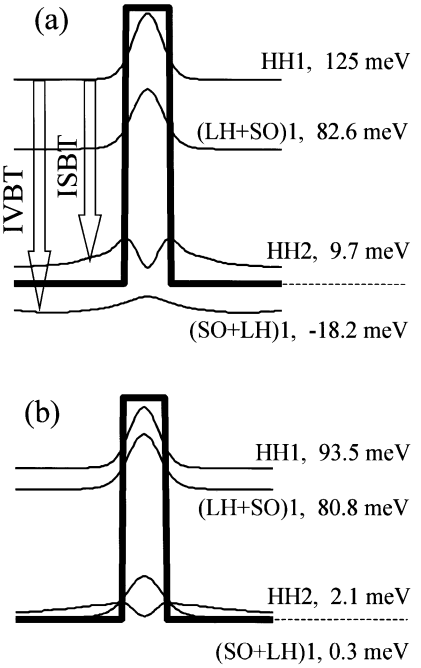

Fig. 3. The square of the envelope wave functions for all bound states at $k_\perp = 0$. (a) Fully strained QW. (b) Fully relaxed QW.

$-(0.09 \pm 0.02)$ eV. In addition, we did not observe a shift of the QW ISBT peak energy while the IVBT lines show a red shift of the peak energy at temperatures above 800°C (see Figs. 2(b) and 3(b) in Ref. [6]).

The high-temperature activation process is assigned to inter-diffusion of Ge/Si atoms between the strained SiGe QWs and the Si barrier regions. This process causes a destruction of the interfaces between the wells and the barriers, giving rise to a strong alloy disorder scattering that destroys the coherency of the QW electronic states. The activation energy measured for this process is in good agreement with other reports on Ge/Si inter-diffusion in strained layers that were detected by other experimental techniques [9,10]. The semi-bulk IVBT (from the wide well) is expected to be less sensitive to this process since inter-diffusion should destroy the entire SiGe region rather than the interfaces (as is in the case of the 30 Å QW).

The mid-temperature activation process is assigned to thermally activated strain relaxation in the pseudomorphic SiGe layers [3,4,11,12]. To verify this assumption we measured the Raman scattering spectra of the samples for each annealing temperature. The inset of Fig. 2(b) shows a typical spectrum obtained at 700°C, with the various phonon lines as indicated in the figure. In Fig. 2(a) we plot the strained Si–Si phonon line versus the annealing temperature. With the increasing temperature the strained Si–Si line shifts towards the bulk Si–Si line, until the two lines can not be resolved above 900°C. Fig. 2(b) shows a red shift of the SiGe phonon line as annealing temperature rises. Here again, two activation processes with activation energies of $\Delta E_S \cong (0.11 \pm 0.04)$ eV and $\Delta E_D \cong (2.3 \pm 0.6)$ eV are clearly observed. These two energies are in good agreement with the activation energies observed for the QW ISBT.

In order to understand the influence of strain relaxation on the valence band structure and the various optical transitions involved in our sample, we numerically solved the 6×6 Luttinger–Kohn (LK) Hamiltonian [13] for our $Si_{1-x}Ge_x$/Si QW structure. In our calculations, we took into account both the confinement potential and the strain deformation potential using the Pikus–Bir Hamiltonian [14]. The solution was derived in a similar manner to that presented in Refs.

[7,8], where a Fourier transform of the envelope wave functions transforms the set of six coupled LK differential equations into an algebraic matrix that can be diagonalized. Both envelope wave functions and energy dispersion relations for all confined levels were numerically calculated.

In Fig. 3 we show the square of the envelope wave functions for all bound states at $k_\perp = 0$. Two limiting cases are shown: a fully strained QW and a fully relaxed QW. These two limiting examples serve the purpose of illustrating how strain affects the band structure. First, for a fully relaxed QW, the gap between HH and LH ground states is strongly reduced (in bulk silicon the two bands are degenerated). Second, the HH QW potential becomes shallower in the absence of strain, thus pushing up the HH2 state near the top of the QW. As a result, the HH2 envelope wave function becomes less localized in the QW region. Third, the strain in the QW gives rise to an additional strong mixture between SO and LH. However, once the energy of the mixed states lies above the LH barrier, the LH contribution becomes unlocalized. As a result, the strain causes the entire envelope wave function to be less localized in the QW as illustrated in Fig. 3. During the relaxation the contribution of the LH becomes smaller and the envelope state become more localized in the QW region.

The above effects are responsible to the activation processes observed by the optical absorption measurements. The energy levels involved in the optical transitions, i.e. HH1 $\rightarrow$ HH2 and HH1 $\rightarrow$ (SO + LH)1, are in good agreement with the experimentally observed absorption spectra. Furthermore, the integrated absorbance of the ISBT is proportional to $|\langle \mathrm{HH1}|z|\mathrm{HH2}\rangle|^2$, where $|\mathrm{HH1}\rangle$ and $|\mathrm{HH2}\rangle$ are the envelope wave functions of the lowest HH states. Hence, strain relaxation causes the HH2 envelope to be less localized in the QW and to a decrease of the absorption as observed in the experiment. The integrated absorbance of the IVBTs is proportional to the envelope states overlap $\langle \mathrm{HH1}|(\mathrm{SO} + \mathrm{LH})1\rangle$ [7,8]. Here, we find that strain relaxation gives rise to a larger degree of envelope state localization. For example, in the two limiting cases shown in Fig. 3 we find that the state (SO+LH)1 consists of 32% SO and 68% LH in the fully strained case while 88% SO and 12% LH is obtained for the fully relaxed structure. Hence, with increasing annealing temperature the contribution of the localized SO to the overlap integral increases giving rise to an increase of the absorption. Note that this model also explains the red shift of the optical transitions [6].

In summary, we have measured the influence of thermal annealing processes on inter-valence band and inter-subband transitions in pseudomorphic $Si/Si_{1-x}Ge_x$ quantum wells. Two thermally activated processes were resolved. The first process is assigned to strain relaxation that gives rise to a decrease of the ISBT and an increase of IVBTs. At temperatures above 940°C a second aprocess of Si/Ge inter-diffusion was observed. This process destroys the coherency of the QW envelope states giving rise to a rapid decrease of all QW absorption lines.

Acknowledgements

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