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Growth Pressure Effects on $Si/Si_{1-x}Ge_x$ Chemical Vapor Deposition

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We studied the effects of growth pressure on $Si_{1-x}Ge_x/Si$ heterostructures grown by rapid thermal chemical vapor deposition in the pressure range of 6–220 Torr. The material was characterized by photoluminescence (PL), x-ray reflectivity, and electrical measurements on resonant tunneling diodes (RTDs). High quality material was demonstrated throughout the pressure range, but a weaker PL intensity at higher pressure (220 Torr) indicates lower lifetimes. Interface abruptness was degraded at higher pressures due to gas transients. This was confirmed by x-ray reflectivity measurements and the performance of RTDs. We have established a low pressure limit to interface roughness of 0.2–0.5 nm, determined by x-ray reflectivity.

Key words: Growth pressure effects, rapid thermal chemical deposition, Si/SiGe

INTRODUCTION

The growth of thin crystalline Si and $Si_{1-x}Ge_x$ layers on Si substrates by low-temperature chemical vapor deposition (CVD) has been extensively studied in recent years, and high quality material and electronic devices made in these films have been demonstrated. These different techniques operate in a wide range of growth pressures, from mTorr to atmospheric pressure. In ultra-high-vacuum CVD (UHV/CVD) reactors, the growth pressure is measured in mTorr range,[1] limited reaction processing[2] (LRP) and rapid thermal CVD[3] (RTCVD) usually operate in the 1–10 Torr range, while atmospheric pressure CVD[4] (APCVD) works at atmospheric pressure. Typically dichlorosilane (SiH_2Cl_2) or silane (SiH_4) is used as Si source and germane (GeH_4) as Ge source. However, there have been no systematic studies reported so far relating the growth pressure to the material characteristics. In this work, we studied the effects of growth pressure on the material quality and interfacial properties of $Si_{1-x}Ge_x$ layers on <100> Si substrates. The material has been characterized by photoluminescence (PL), x-ray reflectivity (XRR), and the performance of resonant tunneling diodes (RTDs).

All samples in this study were grown in a single RTCVD system. In this system, a single 100 mm silicon wafer is suspended on quartz pins inside a 175 mm diameter quartz tube. The total growth chamber volume was ~30 l. The wafer is heated by a bank of tungsten-halogen lamps. All layers were grown with a hydrogen carrier flow of 3 slpm. The hydrogen is purified by diffusion through a palladium cell, and the dichlorosilane is purified by a Nanochem™ cell to

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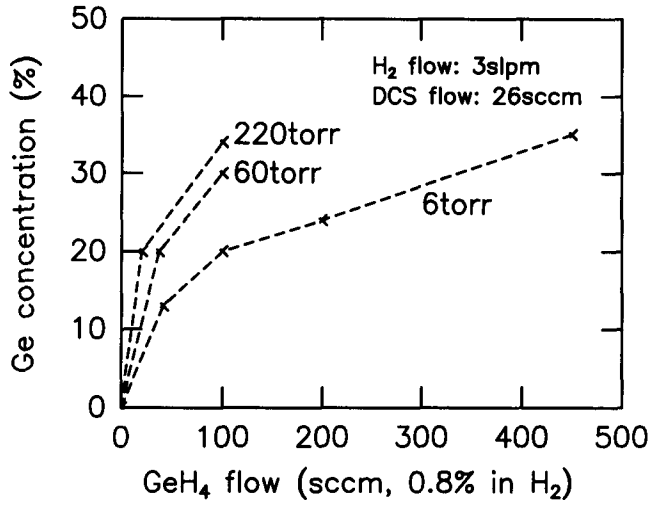

Fig. 1. Ge fraction vs GeH_4 flow for different growth pressures at 625°C. The H_2 was 3 slpm and the dichlorosilane flow was 26 sccm. The uncertainty in Ge fraction is ±2%.

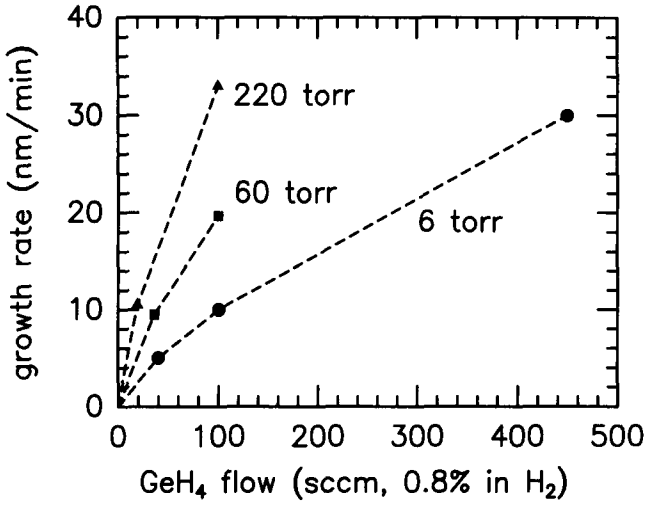

Fig. 2. Growth rate vs GeH_4 flow for the same conditions as in Fig. 1. The uncertainty in growth rate is ±10%.

remove water and oxygen. After an initial one minute clean at 1000°C in hydrogen, a 1 μm thick buffer layer was grown using dichlorosilane. After the buffer layer a thin Si layer was grown at 700°C, and the temperature was then lowered (with dichlorosilane on) to 625°C (unless otherwise noted) for all $Si_{1-x}Ge_x$ growth. The $Si_{1-x}Ge_x$ growth was controlled by turning the GeH_4 source gas (0.8% in H_2) on and off. A run/vent gas line configuration was used so that gas flows in mass flow controllers were stabilized before switching reactive gases into the growth chamber. Note that gas switching, as in conventional CVD, and not temperature switching, as in LRP,[2] was used to start and stop the growth of layers. The growth pressure was varied between 6 and 220 Torr for all layers in each sample. The pressure was increased by an automatically controlled butterfly valve on the input of the process pump. Since the hydrogen carrier was fixed at 3 slpm, this implied a lower gas velocity in the growth chamber at higher pressure. Further details on the reactor can be found elsewhere.[3]

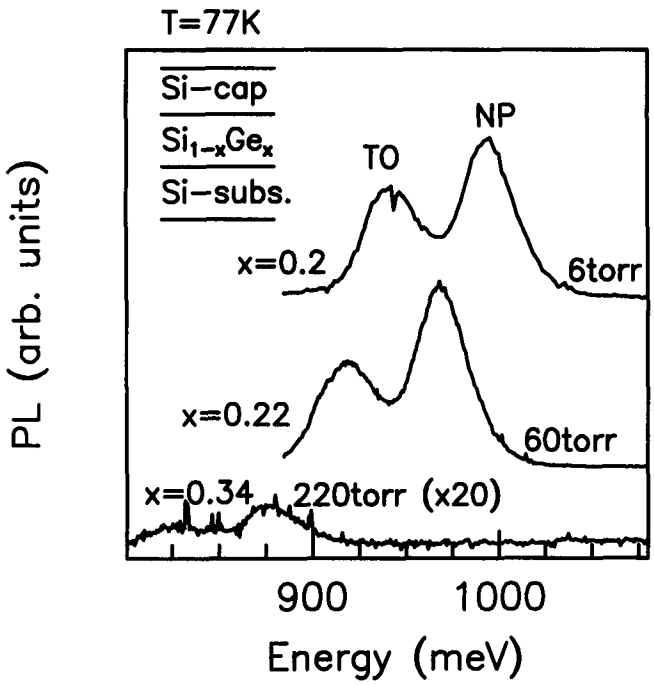

Fig. 3. Typical PL spectra of SiGe samples grown at 6, 60, and 220 Torr. Note the no-phonon (NP) peak and transverse optical (TO) phonon replica indicating band-edge luminescence and low defect concentration.

COMPOSITION AND GROWTH RATE

The composition was determined from the bandgap as measured by photoluminescence (PL). Thin samples were used to avoid strain relaxation (although thicker than 10 nm to avoid quantum confinment effects). The Ge concentration in the alloy layer (x) increased with the increasing GeH_4 flow at a given pressure (Fig. 1). Note however, that the Ge fraction increases with pressure for the same gas flow conditions, even though the dichlorosilane/germane ratio is constant. The reason for this effect is not known.

The growth rate in $Si_{1-x}Ge_x$ layers grown at various pressures was measured by a bevel-and-stain technique on thick test samples and by selective chemical etching and measuring the etch-depth with a stylus profilometer on thin test samples. The resulting growth rates were consistent with those obtained by x-ray reflectivity measurements described later. The growth rate increased monotonically with GeH_4 flow, but it was higher for the same gas flows at higher pressure (Fig. 2). It is interesting to note that the growth rate was similar for the samples with similar Ge content in the solid, regardless of the growth pressure. For example, for a Ge fraction of x = 0.2, GeH_4 source gas flows (0.8% in H_2) of 100, 35, and 19 sccm were required at pressures of 6, 60, and 220 Torr, respectively, but the growth rate in all cases was ~10 nm/min.

PHOTOLUMINESCENCE MEASUREMENTS

Since PL from $Si_{1-x}Ge_x$ layers depends on a low level of nonradiative recombination (high minority carrier lifetimes), photoluminescence is a sensitive probe of material quality.[5] We measured PL spectra on 25 nm

thick, undoped $Si_{1-x}Ge_x$ layers (x = 20–34%) grown at various pressures, with a Si-cap layer of 15 nm to prevent surface recombination. All PL spectra in this study were taken at 77K. A typical PL spectra at 77K shows a no-phonon (NP) feature at higher energy due to alloy randomness, and a lower energy transverse optical (TO) phonon replica (Fig. 3). The energy position of the NP peak is determined by the band-gap of the $Si_{1-x}Ge_x$ quantum well, i.e. the Ge concentration. The purpose of the PL was not to study the fine structure of the NP and TO peaks, which are thermally broadened at 77K, but a qualitative measure of the minority carrier lifetime. The luminescence is inversely dependent on the carrier lifetime, and small amounts of oxygen or other contamination in the SiGe films or at their interface can quickly quench the luminescence by providing a very fast alternative recombination path. All the samples clearly showed these two thermally broadened peaks corresponding to NP and phonon-replica lines, as expected for high quality films. The PL intensity was noticeably weaker for samples grown at 220 Torr, indicating a lower lifetime. This might indicate a higher oxygen concentration in the films grown at 220 Torr. The partial pressures of both oxygen due to source gas contamination and due to outgassing of the reactor walls would be expected to be higher at high pressure. This would lead to higher oxygen levels in the films since the growth rate at a fixed film composition (e.g. x = 0.2) was not a function of growth pressure, as mentioned earlier in the paper.

X-RAY REFLECTIVITY MEASUREMENTS

The interface roughness of SiGe layers was determined by measuring x-ray reflectivity (XRR) using energy dispersive detection. This technique measures interference due to reflections from different layers. The scattering vector (k) is scanned by keeping the scattering angle fixed and measuring the reflected intensity as a function of energy. X-ray reflectivity is sensitive to the gradient in the electron density (dN/dz) normal to the surface so that the measured intensity is proportional to the square of the magnitude of the the Fourier transform of dN/dz. The interface is characterized by a nonuniform electron density profile in the direction perpendicular to the sample surface, i.e. a peak in thc gradient profile. Abrupt interfaces will have a sharper peak in dN/dz, while rough or graded interfaces will exhibit a broader peak. The oscillations in the reflectivity spectrum result from the interference between different layers. The periodicity of the signal is determined by layer thicknesses, and oscillations decay at high k due to nonabrupt interfaces between layers. The amplitude of the signal depends on Ge concentration in the layer. The measured signal was fitted with a model where the interface width, layer thicknesses, and Ge fraction were fitting parameters. The electron density gradient was approximated by Gaussian lineshape. The interface width (σ) was determined by a best fit to the data ($dN/dz \propto e^{-z^2/2\sigma^2}$). Further details on this technique are given elsewhere.[6] This technique does not distinguish between width of the interface due to grading and roughness, as both lead to a gradual transition in electron density.

The samples used for this measurement were the same samples used for measurmg the PL spectra. The $Si_{1-x}Ge_x$ layers were 20–30 nm thick with x = 0.2–0.3, followed by 15 nm Si caps. Typical XRR spectra and

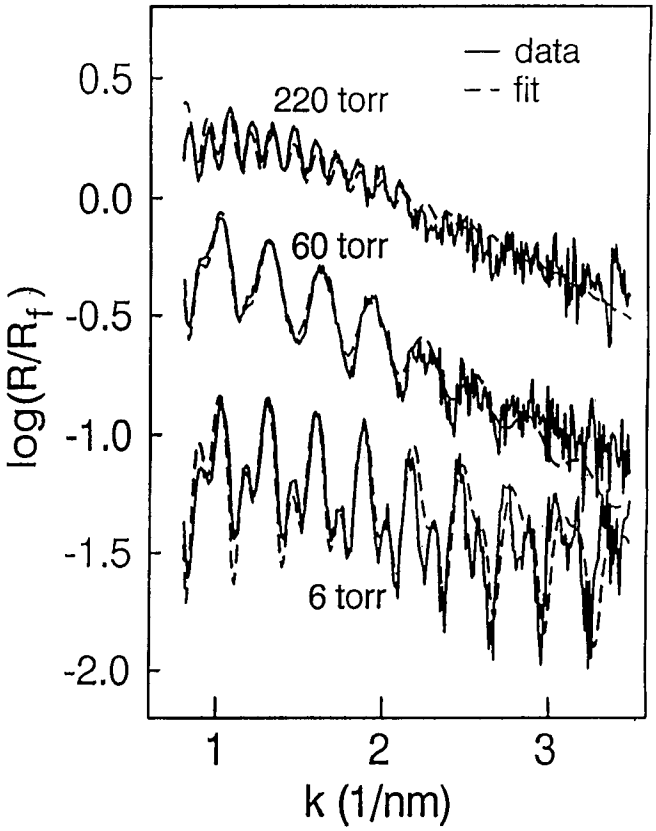

Fig. 4. Typical x-ray reflectivity spectra for samples with single $Si_{1-x}Ge_x$ layers (x = 0.2–0.3, t = 0.2–0.3 nm) with 15 nm Si-caps. The reflected intensity is plotted as a function of scattering vector for different pressures. The solid line represents the data and the dashed line is the best fit.

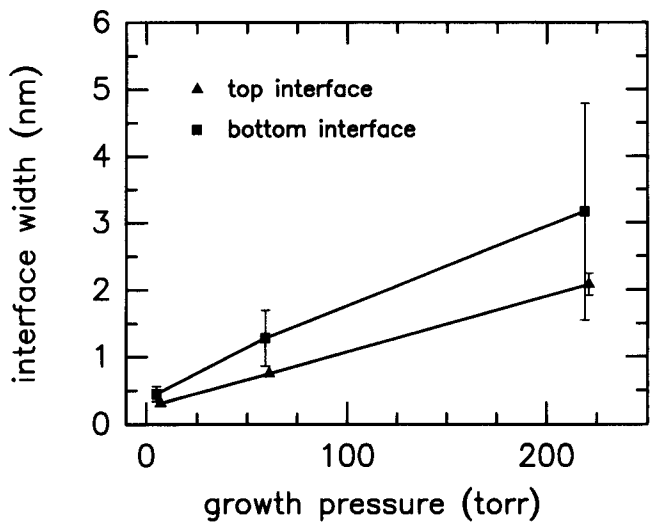

Fig. 5. The interface width of the top and bottom $Si_{1-x}Ge_x$/Si interfaces as a function of growth pressure.

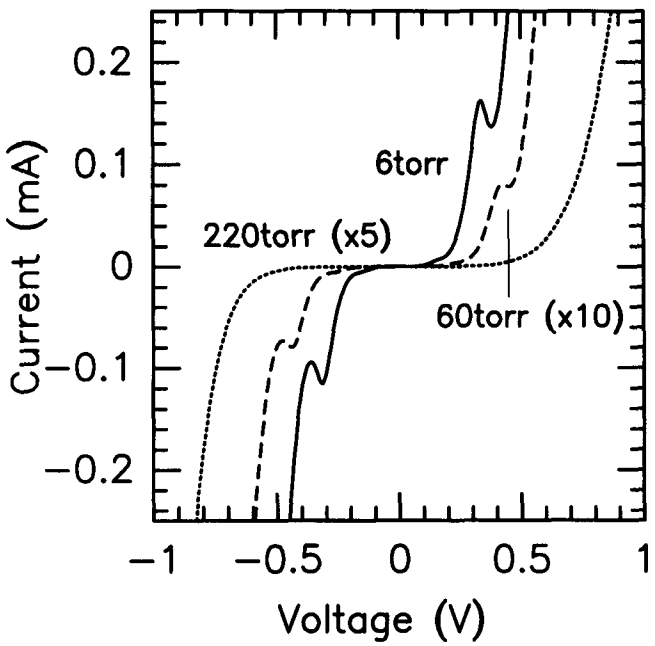

Fig. 6. Resonant tunneling diode I-V curves measured at 80K of samples grown at 6, 60, and 220 Torr. The desired structure was the same in all three samples.

the best fits are shown in Fig. 4, for structures grown at 6, 60, and 220 Torr. Note the faster decay of the oscillations at higher pressures indicating wider interfaces in the high pressure samples.

In all samples, a best fit to the top surface roughness (the surface of the Si cap) was found to be 0.3–0.5 nm, regardless of the growth pressure. This number clearly shows roughness, not grading, since this is the interface between Si and vacuum. The presence of a native oxide on the Si cap was shown to have a negligible effect on the roughness determination by removing it with dilute hydrofluoric acid from some samples. Figure 5 shows the interface width vs growth pressure both for bottom (between the Si substrate and SiGe layer) and top (between the SiGe layer and Si cap) interfaces. No clear dependence of interface widths on Ge concentration in the alloy layer was observed. The interface width was found to linearly increase as the growth pressure was increased, for both interfaces. Despite the error bars in Fig. 5, which were due to uncertainty in fitting the XRR curves, it is also clear that the bottom interface consistently appears to be wider than the upper interface, regardless of the growth pressure.

RESONANT TUNNELING DIODES

Another measure of the interface abruptness quality is the performance of resonant tunneling diodes (RTDs). An RTD consists of a $Si_{1-x}Ge_x$ quantum well sandwiched between Si barriers and symmetrically doped contact layers on both sides. The resulting current voltage (I-V) curve shows a peak in the current when the device is biased such that the bottom of the band filled with carriers in the emitter aligns with the state in the well. When biased further, such that there is no state to tunnel to, the I-V characteristics show negative differential resistance. The performance of RTDs is very sensitive to well and barrier thicknesses and to the quality of the interfaces. Both p and n-type RTDs in $Si/Si_{1-x}Ge_x$ heterostructures have been demonstrated and studied by by several groups.[10–14]

We fabricated p-type RTDs grown at 6, 60, and 220 Torr. The RTD structures consisted of Si p^+ layer (100 nm thick, doped ~5 × $10^{18}cm^{-3}$), undoped $Si_{1-x}Ge_x$ spacer (15 nm thick, x = 0.25), undoped Si barrier, $Si_{1-x}Ge_x$ well, Si barrier, undoped $Si_{1-x}Ge_x$ spacer (15 nm thick, x = 0.25) and finally p^+ Si contact layer (150 nm thick). The nominal barrier widths were 5 nm and well widths were 4 nm. The resulting I-V curves at 80K are shown in Fig. 6. The sample grown at 6 Torr clearly shows negative differential resistance, as expected. Similar behavior is observed in the 60 Torr sample. The sample grown at 220 Torr shows no resonant tunneling behavior at all; rather the I-V characteristics look like that expected for a single barrier. The electrical performance of RTDs is related to XRR interface widths, as explained in the following section.

GRADING AT THE INTERFACE VS ROUGHNESS

The increase in interface widths at higher growth pressures, as measured by XRR, is primarily due to a graded interface from gas transient effects, not to surface roughness. Since the same H_2 carrier flow was used in all experiments (3 slpm), the gas velocity through the chamber is inversely proportional to pressure, and the residence time of gas in the chamber is linear with pressure. A differentially pumped residual gas analyser (RGA) was used to measure the actual rate of change of germane pressure in the growth chamber (although at a location significantly downstream from that of the silicon wafer). At 6 Torr, the time constant for the transient (which was an exponential decay) was 6–7 s, while it was as large as 60 s at 60 Torr. These values are near those one would calculate for simple gas residence times in the chamber given the chamber volume of ~ 30 l and gas flow of 3 slpm. Since the growth rate for a given film compositon was independent of pressure (e.g. ~ 10 nm/min for x = 0.2), the linear increase in gas switching time as pressure is increased would cause a linear increase in the interface width, as is observed in the XRR data. Using the measured gas transients and known growth rates, the calculation of interface width yielded order-of-magnitude agreement with the values measured by XRR.

A second interesting feature in the data of Fig. 5 is that the lower interface seemed consistently broader than the top interface. Because of the low growth temperature of $Si_{1-x}Ge_x$ (625°C), this could not be due to excess thermal diffusion at the lower interface. If one were to explain this interface width as due to the roughness of the growth surface, one would need to assume that the original silicon homoepitaxial surface (before the $Si_{1-x}Ge_x$ growth) were rougher than

the heteroepitaxial $Si_{1-x}Ge_x$ growth surface. Exactly the opposite is observed in practice, however.[7,8] Rather, we think that the possible difference between the two interfaces is due to the dependence of the growth rate on germane flow. The RGA measurement showed that the gas transients had the shape of a decaying exponential, as illustrated in Fig. 7. The growth rate vs time will have a similar shape as the GeH_4 partial pressure, as shown in Fig. 2. The interfacial width will be the integral of the growth rate during the transient period (dashed in Fig. 7). The lower $Si/Si_{1-x}Ge_x$ interface, which occurs when GeH_4 was turned on, has a large part of the transient in a region of high GeH_4 flow and hence high growth rate, leading to a thick graded region. Similarly, the top interface, occuring when the GeH_4 is turned off, has most of its transient during a period of low GeH_4 flow and low growth rate, leading to a sharper interface. From RGA results and Fig. 2, one estimates that the bottom interface should be thicker than the top one by a factor of 1.5–2, consistent with the XRR data.

Therefore, at higher pressures, the interface width is limited by the grading at the interface, due to gas transients, and not the interface roughness. This also explains the behavior of resonant tunneling diodes. According to XRR results, the transitions between the barriers and the well become more diffuse due to grading as growth pressure increased. The interface widths are measured to be only 0.3–0.5 nm at 6 Torr, 0.7–1.3 nm at 60 Torr, but 2–4 nm at 220 Torr. That means that the actual structure grown at 6 Torr is very close to the desired one. At 60 Torr, the double barrier structure is still clearly resolved, since the desired well and barrier widths are still much larger than interface widths. At 220 Torr, the well between the barriers almost disappears leading to a single-barrier structure, consistent with the electrical results shown in Fig. 6. The performance of double barrier RTDs is thus consistent with the results measured by XRR.

LOW PRESSURE LIMIT TO INTERFACE ROUGHNESS

So far, we have demonstrated that high quality $Si_{1-x}Ge_x$ layers can be grown in a wide pressure range; but as the growth pressure increases, the effects of gas transients become more significant because of longer residence time in the chamber. One can estimate the intrinsic roughness of the growth surface, however, by extrapolating the lines in Fig. 5 to zero pressure, where gas transients would be zero. In this case, one finds an interface roughness of 0.2–0.4 nm, similar to the roughness of the top Si surface measured by XRR. This is consistent with the surface roughness of 0.3 nm (rms, measured by atomic force microscopy) of thin $Si_{1-x}Ge_x$ layers reported by Pidduck et al.[8] Similarly, Dutarte et al.[9] have reported an upper limit to interface width of 0.4 nm, resolved from transmission electron micrograph $Si/Si_{1-x}Ge_x$ superlattice.[9]

One can take different approaches to avoid the effect of grading and isolate the upper limit to interface abruptness. Simply lowering the pressure or increasing the carrier gas flow rate to decrease the gas residence time was not possible due to pumping speed limitations in our system. Another possibility would be to turn the growth on and off at interfaces by rapid switching of the sample temperature, as done in limited reaction processing.[2] With no growth occuring during the gas switching, which is done at a very low temperature, the effect of gas transients would be removed. A second approach is to lower the growth temperature, and hence, lower the growth-rate, using conventional gas switching as in our experiments. The interface layer will thus be thinner for the same time of gas transient.

Both methods were used to grow test structures at 6 Torr. For the LRP approach, the growth was interrupted by reducing the lamp power such that the wafer temperature was too low (below 450°C) for growth during germane transient after the $Si_{1-x}Ge_x$ layer was grown at 625°C. The resulting interface widths measured by XRR were 0.3 nm for the top Si/vacuum interface, 0.6 nm for the bottom $Si/Si_{1-x}Ge_x$ interface, but 0.1 nm for the top $Si/Si_{1-x}Ge_x$ interface were the growth was interrupted. These results are consistent within the fitting error of the XRR curves with the low pressure limit extrapolated from the pressure dependent measurements described above.

To further probe the low pressure limit to interface abruptness, the second approach of low temperature growth was also probed. The growth rate at 625°C of $Si_{0.8}Ge_{0.2}$ is 10 nm/min at 6 Torr for our growth conditions. When the temperature is lowered to 550°C, the growth rate drops to only 0.5 nm/min. The measured interface widths for samples grown at 6 Torr and 625°C were 0.3–0.5 nm. If the interface roughness

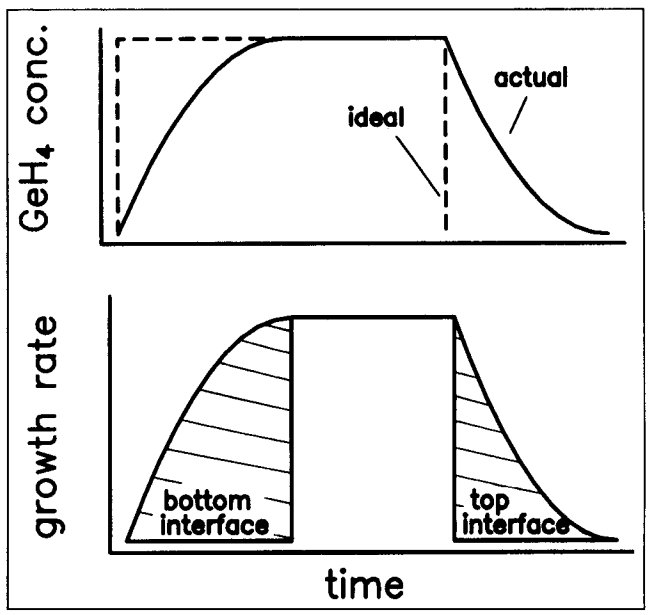

Fig. 7. A schematic diagram that explains the effects of gas switching on the thicknesses of graded layers at the top vs the bottom interface. The thickness of the interface layer is proportional to the cross-hatched area in the lower figure.

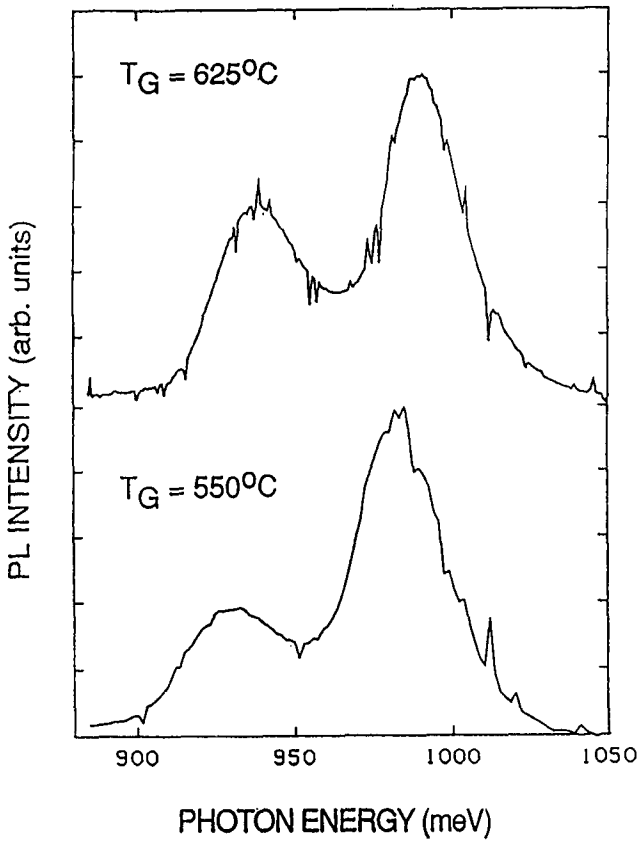

Fig. 8. Photoluminescence spectra at 77K of the single $Si_{0.8}Ge_{0.2}$ quantum wells grown at 6 Torr, 550 and 625°C.

was still degraded by grading, lowering the growth rate during gas transients 20 times would reduce the thickness of the grading due to transients to be negligible. The 77K PL spectrum of the sample where the $Si_{0.8}Ge_{0.2}$ is grown at 550°C is almost identical to the one grown at 625°C with the same Ge content and similar layer thicknesses (Fig. 8), showing the high quality of such layers. The resulting interface widths measured by XRR were 0.3 nm for the top Si/vacuum interface, 0.7 nm for the bottom $Si/Si_{1-x}Ge_x$ interface, and 0.1 nm for the top $Si/Si_{1-x}Ge_x$ interface. Within the experimental error, this is consistent with the low pressure limit of x-ray reflectivity results extrapolated from Fig. 5.

CONCLUSIONS

High quality $Si_{1-x}Ge_x$ layers can be grown by RTCVD from 6 to 220 Torr, at 625°C, although the lifetime in the samples grown at 220 Torr appeared degraded compared to that grown at lower pressure. At higher growth pressures, the growth rate increases and the Ge fraction in the films was higher than at low pressure for the same gas flows and temperature. The interfacial width was found to be strongly degraded by gas transients at higher pressures, the lower interface was affected more than the upper $Si/Si_{1-x}Ge_x$ interface. By reducing the temperature to reduce the growth rate (e.g. 550°C), the effect of gas transients can be removed while high quality layers can still be grown. In this case, an interface roughness below 0.5 nm for x = 0.2 was found.

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