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SiGe/Si quantum wells with abrupt interfaces grown by atmospheric pressure chemical vapor deposition

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Atmospheric pressure chemical vapor deposition has been used to grow SiGe/Si quantum well structures on (001) oriented Si substrates. $SiCl_2H_2$ and GeH_4 were used as reactive gases in a H_2 atmosphere. The hydrogen ambient is shown to greatly facilitate the deposition of quantum wells with abrupt interfaces in the temperature range of 550–750°C. The interface roughness is determined to be less than two monolayers, as shown by X-ray reflectivity, X-ray diffractometry data and the characteristics of resonant tunnel diodes showing a peak to valley ratio of 4.2. Photoluminescence spectra with resolved lines of no-phonon and phonon assisted recombination processes are observed.

Introduction

The successful fabrication of high speed SiGe hetero-bipolar transistors (HBTs) as well as the hope to find luminescence in Si based materials via zone folding in Si/Ge superlattices has fostered the development of low temperature SiGe epitaxy. HBTs with a SiGe-base showing record high f_T and f_{max} values have been fabricated using MBE and CVD methods[1–3]. Generally, the SiGe structures have to be grown at low temperatures to avoid Ge segregation and surface roughening due to islanding[4]. At low temperatures the contamination level with O_2 or water vapor has to be very low to hamper surface oxidation leading to defect formation during growth. Consequently ultra-high vacuum systems such as MBE or UHV/CVD have been exploited, since they provide automatically low contamination levels[5]. Those technologies were therefore first in fabricating high quality Si/SiGe multiple quantum well structures and high speed HBTs. More recently low pressure and even atmospheric pressure (APCVD) processes have been employed. Following the prediction of Smith and Ghidini[6] for oxygen free surfaces, one would expect to achieve only low quality material using this growth technique. The contamination levels of water vapor and O_2 are certainly higher in those systems than the data required for oxygen free Si surfaces under vacuum conditions[6]. However, excellent material has been grown with these techniques as demonstrated by well behaved optical[7], structural[8] and device[9] data. In our work we found evidence that hydrogen plays a key role in low temperature epitaxy at atmospheric pressures. The most important features are the enhanced removal of native oxide from Si surfaces at high temperatures and the inhibition of surface oxidation at growth temperatures for periods of minutes[10] as well as the avoidance of Ge segregation and islanding[11].

In this paper we will discuss the experimental findings concerning the interface roughness of Si/SiGe multiple quantum well (MQW) and heterostructures observed by X-ray reflectivity, atomic force microscopy (AFM) and secondary ion mass spectroscopy (SIMS) in context with a model calculation of the hydrogen coverage of Si surfaces in dependence on growth temperature and hydrogen pressure. The natural advantages of APCVD will be emphasized and selected devices are presented illustrating the excellent control achievable in APCVD processes.

Experimental

A modified commercial reactor was used to grow the Si and SiGe films, a detailed description is given elsewhere[8]. SiH_2Cl_2, GeH_4, AsH_3 and B_2H_6 were used as reactive gases in a H_2 carrier gas. Prior to growth the (001) oriented wafers were dipped in diluted HF (1 : 100) for 3 min and water rinsed for 2 min. The water rinse terminates the surface with about one monolayer of oxygen. The wafers were then loaded into the epitaxial too via a N_2 purged load lock. In the growth chamber the wafers were prebaked for 5 min at 950°C.

Typical growth parameters were partial pressures of 200 Pa for SiH_2Cl_2 and 0–0.7 Pa for GeH_4 leading to Ge concentrations ranging from 0 to 40%. Growth temperatures were adjusted between 600 and 800°C resulting in deposition rates for Si ranging from 0.5 to 80 nm min^{-1}, respectively. Compositional changes from Si to SiGe and vice versa were made by gas switching using brief growth interruptions at the interfaces.

Results and discussion

SIMS profiles of three samples grown at 600, 700 and 800°C containing a thick SiGe layer capped in all cases by a 50 nm wide Si film showed a slope of the Ge profile at the top Si–SiGe interface of 2.5–3 nm/decade. The SIMS data were taken using Ar^+ ions as primary ions at an energy of 10 keV. The steepness

of the Ge profiles at the front and rear edges of the Ge box profile is given by these SIMS parameters, which are found to be most suitable for this investigation[11]. No indication of any Ge segregation is detected by SIMS, in particular the long tail in the Ge concentration towards the surface typically observed in MBE samples grown above 400°C[11,12] is not found.

Closely related to the segregation of Ge is the effect of islanding. The high concentration of mobile Ge at the surface leads to the formation of Ge-rich regions at the surface, as a consequence of considerable surface roughening. The probability of island formation increases with deposition temperature and the desired Ge concentration. We therefore studied the surface morphology of SiGe layers with high Ge content grown at temperatures between 550 and 650°C. The structures contained a 10–20 nm wide SiGe film with 12–40% Ge and were capped with a thin Si layer to prevent native oxide formation at the Si Ge surface. Kiehl *et al*[13] report on a AFM study of the surface roughness of similar structures grown by UHV/CVD at 540°C. They found an increase in the surface roughness with Ge concentration for samples grown at these conditions. Figure 1 shows an AFM picture of the APCVD sample grown at 550°C with a Ge concentration of 40%. A tip with a high aspect ratio has been used in an instrument from Park Analytical instruments. No data processing other than background subtraction was done on the images. The experimental conditions were therefore very close to those published in ref 13. The root mean square (rms) roughness at the surface of an APCVD grown quantum well structure was determined to be less than 0.1 nm, which is a typical value observed in all our samples studied by AFM, independently from the Ge concentration and the growth temperature. The long range structure observed on the surface by AFM is reproducible, it is not noise of the instrument, and can be interpreted as undulations with an amplitude in the atomic range with a periodicity of 100–400 nm. Only a small number of depressions with depth of 0.3–0.6 nm are detected. Compared to the published UHV/CVD data, indicating a rms roughness of 0.235 and 0.946 nm at 35 and 45% Ge, respectively, and a significant amount of surface depression with a depth of 0.5–1 nm, our data suggest a much smaller tendency for islanding and surface roughening towards high Ge contents.

We believe that in the case of APCVD, hydrogen at the surface acts as a surfactant, preventing islanding and segregation of Ge. Indeed the Si surface under APCVD conditions is largely covered with hydrogen even at elevated temperatures. Figure 2 shows the fraction of surface sites occupied by hydrogen as a function of temperature for three different hydrogen base pressures. Thermodynamic equilibrium is presumed and the reaction $H_2(g) + Si$-(empty site) $\Leftrightarrow$ 2HSi(ads) was considered. For the calculation the change in enthalpy due to absorption was estimated to be -56 kcal mole^{-1}[14–16]. The change in entropy due to adsorption of hydrogen on the Si surface was estimated to be the loss of molecular translation amounting to -34 cal kmole^{-1}[17]. Using this assumption the hydrogen coverage in the APCVD is more than 99.9% at 600°C compared to just 50% coverage at UHV/CVD conditions. The amount of unsaturated Si atoms at the surface, which can be attracted easily by oxygen is in the case of APCVD always 2–3 orders of magnitude smaller compared to 1 mtorr. The mechanism of how the adsorbed hydrogen inhibits oxidation is not fully understood, however to first order we speculate that an impinging oxygen atom or molecule does not react with the portion of the surface covered with hydrogen. However, the effect is widely known from the resist of HF dipped, i.e. H passivated, wafers towards oxidation in air. This calculation does not consider the H brought to the surface by the hybrids, GeH_4, SiH_4 or SiH_2Cl_2, and their reaction products. In the case of APCVD their effect on segregation and surface oxidation might be negligible, since the surface is covered by H anyway. In low pressure epitaxial CVD tools they supposed lead to an additional H coverage. Still, a more extensive study of the segregation of Ge in the temperature range of 600–800°C comparing APCVD, uhv/CVD and MBE showed no segregation for APCVD in contrast to MBE and UHV/CVD[11].

The hydrogen protection leads to considerable advantages. Growth interruptions at layers of different composition can be used to optimize the interface abruptness without oxidation of the surface during the growth interruption. The avoidance of dopant[18] and Ge segregation as well as suppression of stress relaxation of subcritical thickness SiGe films even at rather high deposition temperatures are further advantages.

In APCVD the abruptness at the Si/SiGe interfaces is no longer limited by Ge segregation. It is a function of the gas switching sequence and depletion of the components in the gas phase of

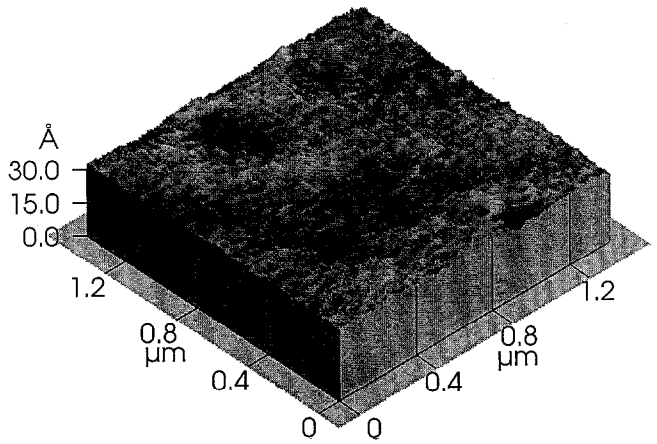

Figure 1. AFM surface image from a $Si/Si_{0.63}Ge_{0.37}$ grown at 550°C, showing monolayer undulations with 100–400 nm periodicity.

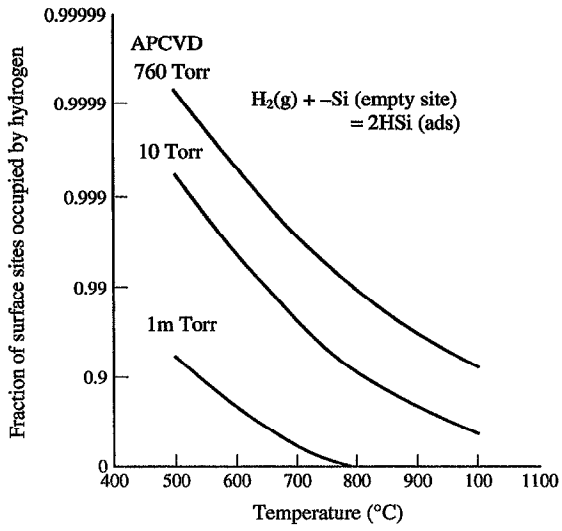

Figure 2. Approximation of the H-coverage of Si surface in dependence on temperature for APCVD and reduced pressure CVD.

the reactor. X-ray reflectivity is particularly suited to study the interface roughness, a detailed description of the methods and the calculation used to determine the inferface roughness is given in ref 19. Figure 3 shows an X-reflectivity measurement taken from MQW structure containing 20 SiGe wells of 1.2 mm width and a Ge concentration of 37% growth at 550°C using optimized gas switching sequences. The rms roughness determined for the Si/SiGe interface is less than 0.2 nm, i.e. less than two monolayers, in agreement with the surface roughness observed by AFM (Figure 1). Similar interface roughnesses have been observed for MQW grown in the temperature range from 500 to 750°C. These results indicate that temperature dependent processes like Ge segregation and islanding are not controlling the interfacial abruptness, moreover, that they are not present in the investigated temperature range and the investigated Ge concentrations below 40%.

The inset in Figure 3 shows well resolved interference peaks between the first and the second reflectivity peaks. Slight fluctuations in the intensity of the interference peaks are noticeable. Simulations of the reflectivity data indicate that they can be attributed to a change in periodicity of a few percent within the MQW structure. Since the thickness of one period is only 3.90 nm, this fluctuation is again in the monolayer range, giving evidence for a high level of control with exact layer to layer reproducibility.

Figure 4 shows the $I(V)$ characteristic of a p-type double barrier resonant tunnelling structure. The active region compromises 5 nm Si barriers cladding a 2.3 nm $Si_{0.75}Ge_{0.25}$ quantum well. On either side of these active regions are undoped $Si_{0.75}Ge_{0.25}$ spacer layers with a grading of the Ge concentration towards the heavily boron doped Si layers at the substrate and the surface of the structure. The inset in Figure 4 depicts schematically the valence band configuration in the active region. The $I(V)$ characteristic shows pronounced resonant current peaks corresponding to heavy and light hole tunnelling with a record high peak to valley ratio of 4.2 : 1. The width of the peak can be used to estimate the interface roughness, since small undulations in well width will shift locally the subband energies of the heavy and light holes

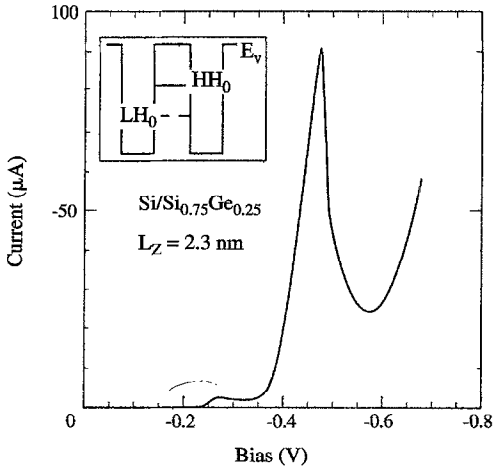

Figure 4. $I(V)$ characteristic at 4.2 K of a DBRTS containing 2.3 nm wide $Si_{0.75}Ge_{0.25}$ quantum well and 5 nm broad Si barriers

leading to a smearing of the resonant tunnelling peak. An exact determination of the interface roughness is difficult due to the effects of the electrical field applied. However, considering the energy shift due to monolayer variations in the 2.3 nm wide well an interface roughness of more than two monolayers across the device can clearly be excluded. A more detailed description of the unique properties of the APCVD grown DBRTS have been published elsewhere[20].

Another indication for abrupt interfaces and exact controllable well width in Si/SiGe quantum wells can be extracted from the optical data of MQW structures. Typically the low temperature (2 K) photoluminescence (PL) spectrum of a SiGe quantum well is assembled of a no-phonon line and four lines associated with phonon assisted recombination processes[21]. This spectrum is also obtained for the SiGe quantum well structures grown by APCVD[22]. The spectrum changes for extremely narrow SiGe quantum wells as displayed in Figure 5. The two PL spectra shown in Figure 5 are taken from samples at 650°C with a Ge

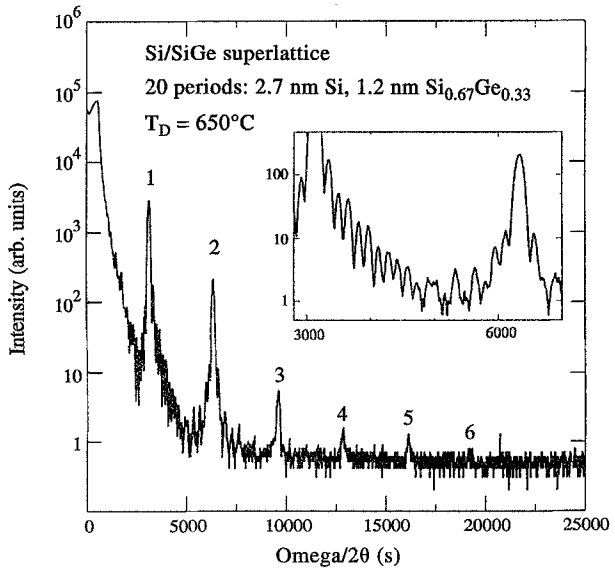

Figure 3. Comparison of experimental and simulated X-ray reflectivity patterns of a SiGe/Si MQW structure deposited at 550°C.

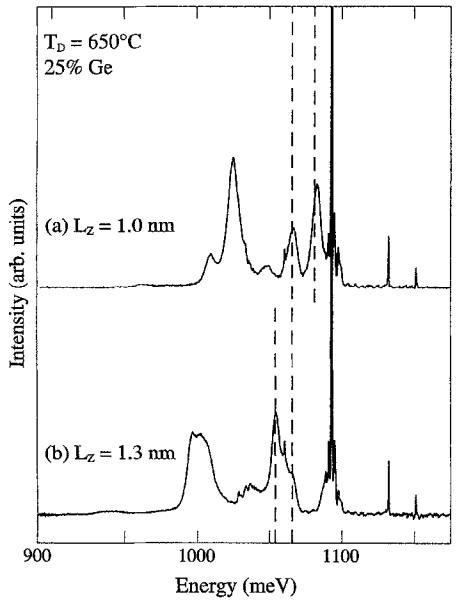

Figure 5. Photoluminescence spectra of MQWs containing 1 nm (top line) and 1.3 nm (bottom line) wide $Si_{0.75}Ge_{0.25}$ wells.

concentration of 25%. The growth parameters were kept constant for both samples except for the growth time per quantum well, which should yield a difference of two monolayers in well width. Sample (a) has a designed well width of 1 nm and sample (b) 1.3 nm. For these well widths we also found the best fit between measured and simulated X-ray diffractometry data. The PL spectra of these samples reveal twice as many peaks compared to PL spectra of thicker SiGe quantum wells. Sample (a) has no-phonon lines at 1065.7 and 1082.4 meV and sample (b) at 1053.8 and 1064.9 meV. These doublets in the PL spectra can be explained either by compositional fluctuations or by different well widths within the sample. A doublet caused by compositional fluctuations should have the broadest splitting for wide quantum wells and should decrease with well width due to the fact that for very narrow quantum wells the heavy hole band merges to the Si band edge independently from the composition of the well. Our experimental observation is the opposite, doublets have not been observed for broad wells and for thin wells the splitting of the doublets increases with decreasing well width. We therefore believe that the doublet is an indication of fluctuations in the well width. The values of the energy splitting of 17.5 meV for sample (a) and 11.1 meV for sample (b) correspond to the expected shift in energy due to a change in well width of one monolayer. Moreover, the two spectra have a common line at about 1065 meV, which is the weaker line in both spectra. This suggests a difference in well width between samples (a) and (b) of two monolayers, in agreement with the difference in well width expected from the growth parameters. We therefore assign the lines of the doublets in the PL spectra to areas within the well which differ by one monolayer, indicating atomic steps at the interfaces comparable to the observation made at perfectionized AlGaAs/GaAs and InP/GaInAs quantum wells.

Conclusions

We have reported on the role of hydrogen for low temperature epitaxial growth of Si/SiGe structures. At a hydrogen pressure of 1 atmosphere in the APCVD epitaxial reactor the surface is covered almost completely by hydrogen in the temperature range of 600–800°C in contrast to very low pressure systems where the surface is largely free from hydrogen. This high surface hydrogen coverage in APCVD greatly facilitates the inhibition of surface oxidation during growth interruptions and avoids Ge segregation during formation of abrupt Si/SiGe interfaces.

Our detailed analysis of hetero-multiple quantum well and resonant tunnelling structures provides evidence of interface roughnesses in the monolayer range. The growth process is easy to control in terms of gas switching sequences, leading to reproducible growth of sophisticated Si/SiGe quantum structures.

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