Extended Abstracts of the 1993 International Conference on Solid State Devices and Materials, Makuhari, 1993, pp. 407-409

Optical Detection of Interdiffusion in Strained $Si_{1-x}Ge_x/Si$ Single Quantum Well Structures

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Interdiffusion at $Si_{1-x}Ge_x/Si$ heterointerfaces has been investigated by applying photoluminescence (PL) spectroscopy to strained $Si_{1-x}Ge_x/Si$ single quantum wells (SQW's) undergoing vacuum annealing. Diffusion coefficients are evaluated by analyzing the observed PL peak energy blue-shifts. The activation energy is found to be 2.47eV±0.4eV. Anomalous peak red-shift was observed by N_2 annealing which is probably the result of surface oxidation. Post-growth annealing was found to improve crystal quality, observed as the dramatic increase in PL intensity. Structural stability was assessed by observing the lower energy PL spectrum, in which dislocation related luminescence due to strain relaxation was hardly observed even after 900°C annealing.

1. Introduction

$Si_{1-x}Ge_x/Si$ strained-layer heterostructures are attracting considerable attention because of their promising possibility for opto-electronic device applications[1] and their versatility of utilizing the established Si integrated circuit processing techniques. Understanding of thermal stability of the structure is a critical issue because high temperature processing may trigger interdiffusion and strain relief which can affect device performances. In this work, we present the first luminescence study on interdiffusion in strained $Si_{1-x}Ge_x/Si$ single QW's (SQW's) undergoing post-growth thermal treatment and show that the diffusion coefficients (D's) can be accurately determined by PL measurements.

2. Experimental

The samples studied were strained $Si_{1-x}Ge_x/Si$ SQW's grown by a purpose-built gas-source molecular beam epitaxy (GSMBE)[2] (Daido Sanso VCE-S2020) on Si(100)p substrates at 700°C. Post-growth annealing was performed either in ultra high vacuum of 4×10^{-10} Torr or in a flowing N_2 gas ambient of 3.0 l/min and the annealing temperatures, T_a's, ranged from 800 to 950°C. PL was measured at 20K in standard lock-in configuration with an Ar^+ ion laser and a liquid-nitrogen-cooled Ge detector.

3. Results and discussion

In Fig.1 we plot the PL spectra of the samples with Ge composition x=0.16 and well width L_z=73Å annealed in vacuum for 20 minutes at different T_a's, together with the PL spectrum of the as-grown sample. The observed features are the no-phonon (NP) interband transition due to alloy disorder scattering, and its transverse-optical (TO) and -acoustic (TA) replicas[3]. As can be clearly seen from the spectra, PL peaks are shifted to higher energies and their absolute intensities are enhanced by a factor of 3. The energy shift increases with increasing T_a and the blue-shift can be attributed to potential modulation induced by the interdiffusion of Si and Ge at the $Si_{1-x}Ge_x/Si$ interfaces.

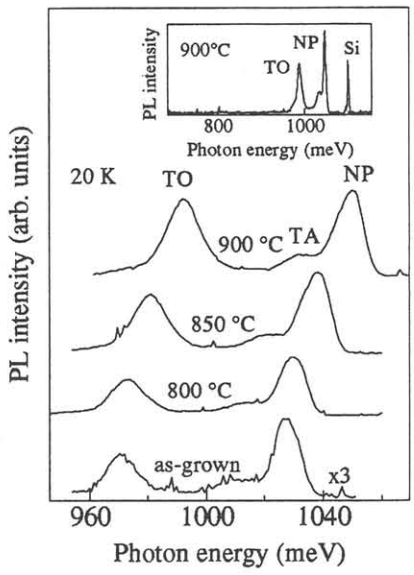

Fig.1 PL spectra of strained $Si_{0.84}Ge_{0.16}/Si$ (L_z=73Å) SQW's annealed in vacuum at respective temperatures. Inset is the PL spectrum of the 900°C-annealed sample covering a wider photon energy range.

The inset of Fig.1 shows the lower energy PL spectrum of the 900°C-annealed sample. Strain relaxation by formation of misfit dislocations seems unlikely to have occurred, since deep-level luminescence lines[4] are totally absent in the spectrum and also no cross hatches could be seen by Nomarski microscopy[5]. Hence we can conclude that these SQW's are thermally stable in the temperature range studied. The same trend was confirmed in SQW's having Ge content of up to x=0.2 and well width as thick as L_z = 300Å.

Figure 2 summarizes the PL peak energy shifts observed in the vacuum annealed samples (open circles) as a function of the inverse of T_a's. Also shown are the results of the N_2 annealing experiment (solid circles) carried out for comparison. First of all, let us discuss the results of the vacuum annealing, in which the amount of the energy blue-shift corresponds to the degree of interdiffusion. In order to evaluate interdiffusivity from the energy shifts, we assumed an isotropic diffusion of Si and Ge at both $Si_{1-x}Ge_x$/Si interfaces, and D independent of the Ge composition. The calculation procedure is as follows. Starting with an abrupt square potential profile, which is obtained by GSMBE growth[2], the distorted potential profile is calculated by solving the one-dimensional (1D) diffusion equation. The excitonic luminescence energies of the modulated QW were then calculated by numerically solving the 1D Schrödinger's equation within the framework of the effective mass approximation. Thus by defining a D, one can calculate the emission energy of the distorted QW. The D was varied until the calculated energy shift was within 0.1meV of the experimental value.

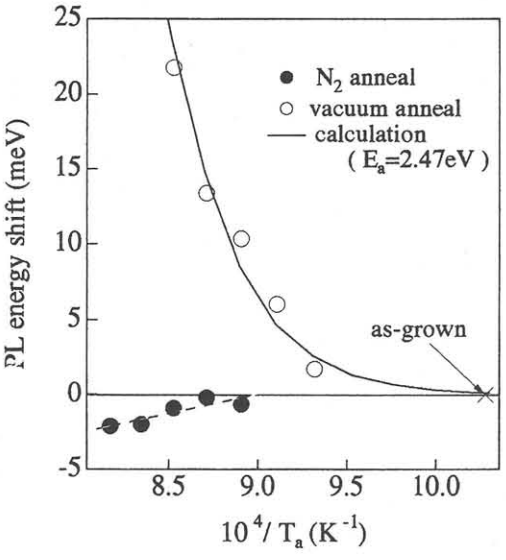

Fig.2 PL emission energy shift with respect to the as-grown sample against the inverse of the annealing temperatures, T_a's; in vacuum (open circles) and in N_2 (solid circles). The solid line is the theoretical fit using the diffusion activation energy of 2.47eV. The dotted line is eye guide for the N_2 anneal.

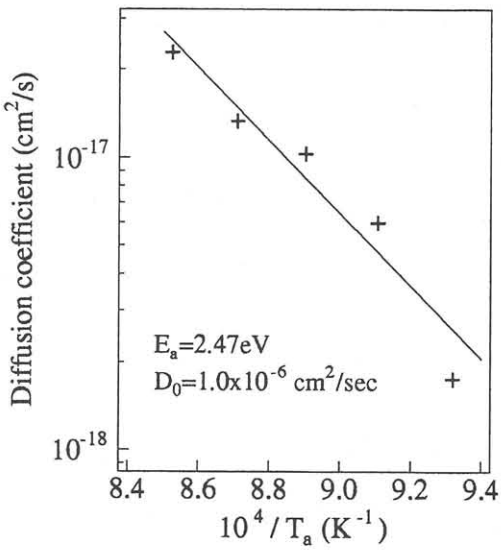

Fig.3 Diffusion coefficients obtained from the PL emission energy shift as a function of the inverse of the annealing temperatures.

Figure 3 shows the calculated D's as a function of 10^4 / kT_a. The D's are seen to follow an Arrhenius behaviour closely and from the linear fit to the data, an activation energy of 2.47eV±0.4eV is obtained. This activation energy seems to be small as compared to what have been reported in previous works, 4-5eV[6], obtained mainly from X-ray diffraction and Rutherford backscattering spectroscopy. On the other hand, the values reported by Baribeau *et al.* were around 2eV[7] which is fairly close to the present value. One possibility for this discrepancy is the fact that the activation energies are rather dependent on the annealing temperature range studied. Since those reports are based on experiments that are rather insensitive to a slight initial change in the Ge profile and thus requires higher T_a and longer annealing time, those samples studied may have gone through strain relaxation during annealing. Therefore, the activation energy obtained here is more reliable for the initial modulation of the Ge profile. A further detailed study is required to abridge the gap between the scattered data.

Returning to Fig.2, we note that the PL emission energies are shifted towards lower energies by annealing in N_2 ambient. This anomalous trend cannot be accounted for by the interdiffusion mechanism mentioned above. We attribute this red-shift to the strain originating from the oxidation of the capping layer by the residual O_2 in the N_2 gas. Recently, there have been several reports on Si band-gap shrinkage due to tensile stress arising at the boundary of Si and growing SiO_2 layers in planarly[8] or locally[9] oxidized structures. A similar mechanism seems to take place in our N_2-annealed samples. This speculation was confirmed by mixing O_2 into N_2 , where the red shift was found to increase with increasing O_2 fraction.

As mentioned earlier, PL intensity was enhanced by a factor of 3 in the vacuum-annealed samples. This fact suggests that the post-growth thermal treatment improves the crystal quality, i.e., eliminating the adverse nonradiative centres[10] for photoexcited carriers. The T_a dependence of the ratio between integrated PL intensity (I_{pl}) from the SQW and that from the Si substrate which is plotted in Fig.4(a) clearly illustrates this idea. It is readily seen that the ratio increases with increasing T_a with a saturation tendency. This can be regarded as the improvement in internal emission efficiency of the QW by the thermal treatment. This is also evidenced by studying the excitation power (I_{ex}) dependence of the I_{pl}, which is plotted in Fig.4(b). It can be seen that although I_{pl} from both the 900°C-annealed and the as-grown sample increase linearly (m=1) with respect to the I_{ex}, the annealed sample seems to saturate at lower I_{ex} than the as-grown sample. Since saturation in I_{pl} is the result of band-filling[11] due to the long decay lifetime of the constituent indirect materials, the annealed sample is likely to be under higher effective excitation as a result of decrease in nonradiative recombination. These findings clearly indicate that the annealing process improves the crystal quality.

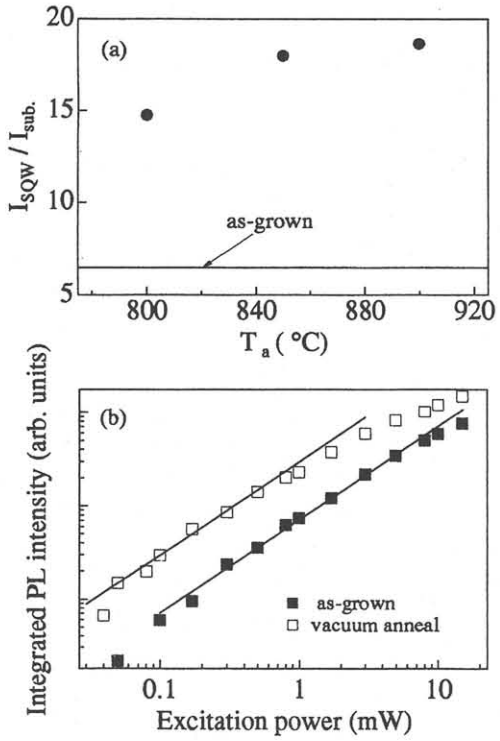

Fig.4 (a) The ratio of the integrated PL intensity between the SQW and the Si substrate as a function of the inverse of the annealing temperatures.

(b) Excitation power dependence of the integrated PL intensity of the as-grown sample and the sample annealed in vacuum at 900°C. The solid line indicates the linear dependence, i.e. m=1.

4. Conclusions

We have determined the interdiffusivity of Si and Ge in strained $Si_{1-x}Ge_x$/Si SQW's by photoluminescence spectroscopy. From the emission energy blue-shifts observed in the vacuum annealed samples the diffusion coefficients were accurately determined. The activation energy was found to be 2.47eV±0.4eV. In contrast, anomalous red-shift was observed by N_2 annealing, which is probably the result of strain originating from the oxidation of the thin capping layer. Dramatic enhancement in the absolute PL intensity was observed in the annealed samples, indicating the improvement in crystal quality. Strain relaxation was hardly observed even after annealing at 900°C, indicating the structural stability of the SQW's of $x \leq 0.2$ and $L_z \leq 300$Å. All these results hold appreciable promise for future device applications.

Acknowledgements

The authors would like to thank H. Yaguchi for valuable discussions and Y. Shimooka and S. Ohtake for their technical assistance. We also acknowledge R. Ito for encouragement throughout the work.

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