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Invited

In-Situ Control of Strained Heterostructure Growth

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The surface exchange reaction of group V atoms is monitored *in-situ* by surface photo-absorption (SPA) during metalorganic vapor phase epitaxial growth of pseudomorphic InAs/InP heterostructure on (001) InP substrates. By selecting the optimum arsine flow and substrate temperature on the basis of SPA monitoring, the As/P exchange reaction in InAs-on-InP growth is suppressed to less than 0.1 monolayer. In contrast, P/As exchange in InP-on-InAs is negligibly small. Pseudomorphic InAs/InP single quantum wells with 1- to 12-monolayer InAs wells are grown using *in-situ* control by SPA. Characterizations by cross-sectional transmission electron microscopy and photoluminescence show the formation of a metallurgically abrupt and atomically flat strained heterointerface. Photoluminescence excitation measurement for an 8-monolayer InAs well shows an energy splitting as large as 0.4 eV between heavy and light holes, indicating that the InAs well layer is coherently strained to the maximum extent within the critical layer thickness.

The formation of an atomically abrupt and flat heterointerface is absolutely necessary for investigating the physics of the heterostructures and for developing heterostructure devices. Methods of growing a heterostructure containing two (or more) different group III atoms such as GaAs/AlGaAs are well developed, but heterostructures containing different group V atoms such as InGaAs/InP have not yet achieved an abrupt and flat heterointerface. During the growth, the surface group V atoms are easily substituted by impinging group V atoms of a different kind to minimize the surface energy by forming the most stable chemical bond. This exchange reaction deteriorates the metallurgical abruptness of the interface by creating short-range roughness. So far, the abruptness of the heterointerface has been studied mainly by *ex-situ* characterizations such as photoluminescence (PL), X-ray diffraction (XD), and transmission electron microscopy (TEM). *In-situ* monitoring and control of the surface exchange reaction during the heterostructure growth would enable us to clarify its mechanism and quickly determine the appropriate growth conditions for obtaining an abrupt and flat heterointerface.

In this work, we used surface photo-absorption (SPA) [1] to monitor and control *in-situ* the exchange reaction at the heterostructure growth. We chose the pseudomorphic InAs/InP system (3.2% lattice mismatch) as a heterostructure containing different group V atoms. This system is a promising strained heterostructure for 1- to 1.5-μm optoelectronic devices[2], but conventional growth methods and conditions have not been able to grow high-quality quantum wells consisting of more than four InAs monolayers (MLs). We grew InAs/InP single quantum wells with 1-12 MLs of InAs as a result of using *in-situ* control, and verified the benefits of *in-situ* control by characterizing the quantum wells by TEM, PL, and photoluminescence excitation spectra (PLE).

The conditions for MOVPE growth and for SPA monitoring were the same as previously reported[3]. A typical SPA reflectivity change observed when AsH_3 was supplied onto the In surface of (001) InP followed by As desorption is shown in Fig. 1[3]. The surface reaction for each SPA signal regime is illustrated. The substrate temperature was maintained at 400°C. First, P-stabilized surface was formed by the supply of PH_3 to the InP surface. When the PH_3 supply was stopped, the reflectivity gradually increased due to P desorption from the InP surface, and finally saturated. This saturated surface is the In surface of InP. Next, a total of 2 μmol of AsH_3 was supplied onto the In surface. This caused a decrease in reflectivity because the In surface became stabilized by As atoms. Then, when the AsH_3 supply was stopped, the reflectivity increased and saturated as In surface was formed again by As desorption. The reflectivity level of the In surface after As desorption was higher than that prior to AsH_3 exposure. This result indicates that, while the InP surface is exposed to AsH_3, the substitution of P by As atoms occurs on the InP

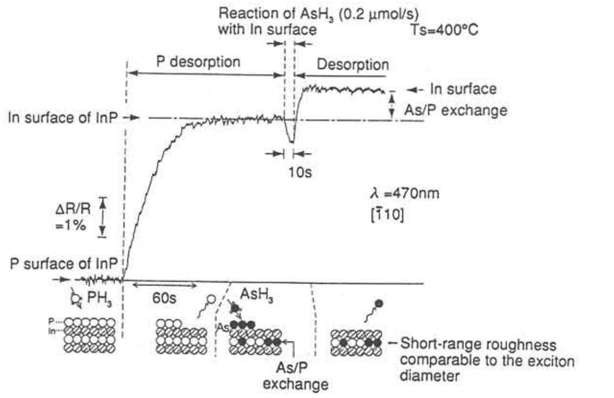

Fig. 1. Typical SPA reflectivity change, when AsH_3 was supplied onto the In surface of (001) InP, followed by As desorption.

surface, and, as a result, $InAs_xP_{1-x}$ is formed on the top surface layer. The difference in reflectivity is caused by the change in surface photo-absorption between InP and $InAs_xP_{1-x}$ surfaces.

By assuming that the As/P exchange occurs within only one monolayer of the surface, the exchange ratio can be approximately estimated by comparing the reflectivity change caused by the exchange reaction against the reference, which is the difference between In surface of 1-ML monolayer InAs grown on InP at 350°C and In surface of InP before InAs growth. The reference corresponds to 100% As/P exchange. From the Arrhenius plot of the estimated As/P exchange ratios, in the condition of 0.2 μmol/s AsH_3 supply for 10 s on the InP surface, the exchange reaction proceeded to 44% at 400°C. As the substrate temperature decreased, the exchange ratio decreased with an activation energy of 1.26 eV. The exchange reaction was suppressed to less than 10% at 350°C. The same analysis was done for the P/As exchange in InP-on-InAs growth. The P/As exchange was negligible (<10%) and independent of substrate temperature.

It has been suggested that, in the InAs/InP system, the As/P exchange reaction will induce short-range roughness with a period smaller than the exciton diameter, resulting in a shift in emission energy to a longer wavelength and slight broadening of the PL spectra[4,5]. From the study for the dependences of PL peak energy on the AsH_3 exposure time and flow rate, we found that the exchange reaction also depended on AsH_3 exposure time and flow rate. Therefore, it is necessary to minimize the AsH_3 flow rate and exposure time within the conditions for obtaining As-stabilized surface at InAs-on-InP heterogrowth to suppress the As/P exchange reaction.

To verify the benefit of *in-situ* control and the formation of an atomically abrupt and flat interface by the suppression of the As/P exchange reaction, we monitored *in-situ* the growth of pseudomorphic InAs/InP QWs on (001) InP substrate and characterized them by TEM, XD, PL, and PLE. A typical SPA reflectivity change during SQW growth of a 5-ML InAs well is shown in Fig. 2. The InAs well layer was grown by atomic layer epitaxy (ALE) in order to control the well thickness precisely with an integer number of monolayers. The growth temperature was 350°C. The SPA reflectivity oscillated five times between the level for the CH_3-terminated surface and that for the As-stabilized surface, which corresponds to five monolayers of InAs growth. The As/P exchange ratio can be estimated from the reflectivity of the first As-stabilized surface and the information can be quickly fed back to the growth conditions of AsH_3 flow rate and exposure time in order to suppress the As/P exchange reaction. We can also determine the conditions for producing a metastable CH_3-terminated surface. During the well-layer growth, the background SPA reflectivity increased with increasing InAs thickness. This is due to the higher refractive index of InAs than InP.

Figure 3 shows a cross-sectional TEM photograph of 8-ML InAs/InP SQW grown by *in-situ* controlled MOVPE. So far, using conventional methods, it has been difficult to grow a structure without any exchange reaction and free of three-dimensional nucleation[4,5]. The well thickness measured from the photograph agrees well with the nominal value determined from the growth cycles in ALE. The upper and lower heterointerfaces have atomically abrupt and flat interfaces free of dislocations. The *in-situ* controlled growth at low substrate temperature suppressed both the As/P exchange reaction at the lower interface and strain-induced three-dimensional nucleation at the upper interface. In contrast, a small density of dislocations was observed in 12-ML InAs/InP SQW. From these results, we determined that the critical layer

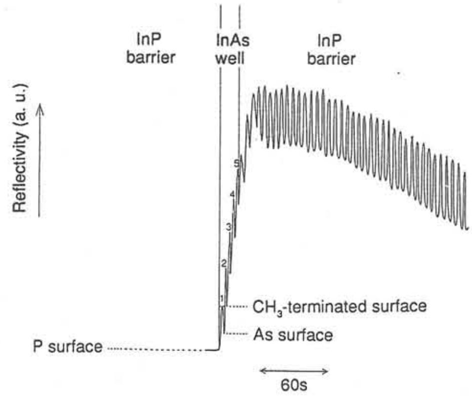

Fig. 2. Typical SPA reflectivity change during InAs well layer growth.

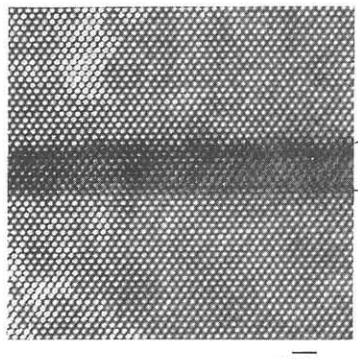

Fig. 3. Cross-sectional TEM image of InAs/InP SQW with an 8-ML InAs well.

thickness of InAs on InP is in the range of 3.0-3.6 nm. This value is compatible with the force balance model[6].

Low temperature PL and PLE measurements were performed to characterize the interface and to investigate the valence band structure of pseudomorphic InAs/InP SQWs. Theoretical calculation predicts that strain splits the degeneracy at the top of valence band, resulting in a lower effective mass for holes. PL and PLE spectra at 11 K for an 8-ML InAs well are shown in Fig. 4. A 100-W halogen lamp was used as the excitation source. The intensity was approximately 10 $\mu W/cm^2$. The detector was a Ge p-i-n photodiode. A single intense, relatively narrow emission line with an FWHM of 18.5 meV was observed in the PL spectra, indicating that long-range roughness as well as short-range roughness is well suppressed and that the density of non-radiative recombination centers at the interface is small. Three peaks (1.39 μm, 1.18 μm, and 0.95 μm) were observed in PLE spectra. We measured the polarization dependence of PLE spectra by TE (incident light polarized parallel to the well layer) and TM (perpendicular to the well layer) mode excitation in order to distinguish

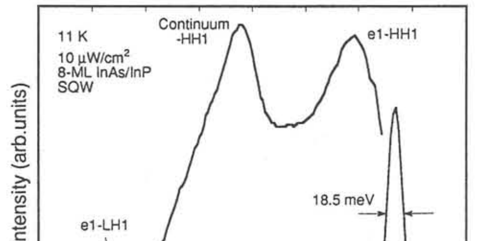

Fig. 4. Low temperature (11 K) PL and PLE spectra of InAs/InP SQW with an 8-ML InAs well.

between the light-hole- and heavy-hole-electron transitions. As a result, the peaks at 1.39 μm and 0.95 μm were respectively attributed to be heavy-hole(hh1)-electron(e1) and light-hole(lh1)-electron(e1) transitions. Furthermore, from the dependence of PLE peak emission energies on InAs well thickness, the peak at 1.18 μm was attributed to be the heavy-hole(hh1)-InP conduction band continuum transition. A large energy splitting of about 0.4 eV was observed between heavy and light holes. This indicates that the InAs well layer is coherently strained to the maximum extent within the critical layer thickness, and suggests that there will be a reduction of the heavy-hole mass and a reduction of the density of states at the top of the valence band. Therefore, InAs/InP SQWs is a promising material for semiconductor lasers with a low threshold current.

During the pseudomorphic InAs/InP heterostructure MOVPE growth, containing two different group V atoms, the surface exchange reaction was monitored *in-situ* by SPA. By adjusting the substrate temperature, arsine flow rate, and exposure time on the basis of the SPA monitoring, the As/P exchange reaction during InAs-on-InP growth was suppressed to less than 0.1 monolayer at 350°C. Pseudomorphic InAs/InP SQWs having 1-12 MLs were grown on (001) InP substrates as a result of this *in-situ* control. Characterizations by TEM, and by PL and PLE measurement showed that the InAs/InP heterostructures were atomically abrupt and flat. PLE measurement also showed a large splitting between heavy and light hole energy bands, indicating that the InAs well layer is coherently strained as expected.

Acknowledgments

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