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Ordering Reduction in $In_{0.5}Ga_{0.5}P$ Grown by Solid Source Molecular Beam Epitaxy

Yi-Cheng CHENG*, Kuochou TAI, Shu-Tsun CHOU[1], Kai-Feng HUANG[2] and Shun-Lih TU[3]
Institute of Electro-Optical Engineering, National Chiao-Tung University, HsinChu, Taiwan 300 , R.O.C.
[1]*Department of Electrical Engineering, Chung Cheng Institute of Technology, Tahsi, Taoyuan, Taiwan 33509, R.O.C.*
[2]*ElectroPhysics Department, National Chiao-Tung University, HsinChu, Taiwan 300, R.O.C.*
[3]*Material R & D Center, Chung Shang Institute of Science and Technology, Taoyuan, Taiwan 325, R.O.C.*

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$In_{0.5}Ga_{0.5}P$ grown on GaAs substrates with different tilting angles by solid source molecular beam epitaxy (SSMBE) is studied. The results showed that a weak ordering effect still exists in SSMBE grown epilayers with tilted substrates. However, the ordering effect can be drastically reduced by growing $In_{0.5}Ga_{0.5}P$ on a 15° tilted substrate with an InAlP/InGaP superlattices (SL) buffer layer. The $In_{0.5}Ga_{0.5}P$ epilayer grown by this method showed a peak photoluminescence (PL) energy of ∼1.91 eV at room temperature, which is similar to the reported value for a fully disordered sample. The intensity of the ordering effect is characterized by polarized PL spectroscopy, and the reduction in the ordering intensity is attributed to the elimination of initial surface strain by the SL buffer layer.

KEYWORDS: SSMBE, InGaP, ordering, SL, polarized PL

1. Introduction

The growth of ternary semiconductor compounds on binary substrates has a tendency towards atomic ordering due to the differences of atomic size and bonding energy.[1,2] For instance, in the case of $In_xGa_{1-x}P$ growth on a GaAs substrate, when the Ga atom impinges on the GaAs surface, the Ga atom locates the nucleation site without any problem. However, if both Ga and In atoms are on the GaAs surface, it is more difficult for the In atom to locate the proper nucleation site due to its smaller bonding energy and relatively larger atomic diameter compared to those of the Ga atom. Therefore, a strong surface strain can be generated with the simultaneous nucleations of Ga and In atoms on the GaAs substrate. This surface strain will either initiate the In surface segregation[3] or a spontaneous atomic ordering in the epilayer. The atomic ordering is thought to be a relaxation effect of surface strain and results in the bandgap reduction due to the atomic rearrangement.[4] Bandgap reduction due to the atomic ordering is generally observed in $In_xGa_{1-x}P$ epitaxial layers grown on a GaAs substrate, and the result has limited the applications of $In_xGa_{1-x}P$ related photonic devices in shorter wavelength ranges. Therefore, it is important to suppress the spontaneous ordering effect in $In_xGa_{1-x}P$ related materials.

Recently, the growth of $In_{0.5}Ga_{0.5}P$ on tilted substrates has proven effective for suppressing the ordering effect in metalorganic chemical vapor deposition (MOCVD).[5] With the growth temperature generally lower than that in MOCVD, $In_{0.5}Ga_{0.5}P$ epilayers grown by molecular beam epitaxy (MBE) have been predicted to have a lower ordering effect intensity,[6] however, spontaneous ordering is still being observed in $In_{0.5}Ga_{0.5}P$ epilayers grown by gas-source MBE (GSMBE).[7] Therefore, in this report, we compared the effect of growing $In_{0.5}Ga_{0.5}P$ on tilted GaAs substrates by solid source MBE (SSMBE) using a phosphorus-valved cracker with samples grown by MOCVD and GSMBE. However, a short-term transient of In flux was observed on our Riber-32P MBE system as a result of radiative cooling of the evaporating surface after opening the shutter of the In cell. Therefore, we used the InAlP/InGaP superlattice (SL) buffer layers prior to the growth of the $In_{0.5}Ga_{0.5}P$ epilayer to eliminate the initial In transient. We noticed that the bandgap energy was remarkedly increased in the $In_{0.5}Ga_{0.5}P$ epilayer with the SL buffer. We attribute this effect to the surface strain reduction by the growth of the SL buffer layer, with a mechanism similar to the defect suppression effect of SL layers in the lattice mismatched epitaxy observed by another group.[8,9]

2. Experimental

Prior to the growth of $In_{0.5}Ga_{0.5}P$ epitaxial layers, white phosphorus was generated by heating a red phosphorus cell to 350°C and allowing the vapor to condense. The red phosphorus evaporator was held at room temperature during the growth period. At the start of white phosphorus generation, 6 hours of red phosphorus evaporator heating can result in the growth of $In_{0.5}Ga_{0.5}P$ of more than 12 μm. After 150 μm growth of phosphorus containing layers, the white phosphorus conversion efficiency was decreased. The reason for the lower conversion efficiency is probably due to the fact that allotrope-like black phosphorus was generated during the heating of the red phosphorus and coated around the wall of the evaporator cell. The change of the condenser volume due to the black phosphorus coating lowers the white phosphorus conversion efficiency. $In_{0.5}Ga_{0.5}P$ epilayers were grown by SSMBE on (001)A GaAs substrates tilted from the [001] direction toward the [110] direction. Four tilted GaAs substrates with different tilting angles, 0°, 3°, 10°, and 15°, were mounted side by side on a 3 inch molybdenum block with high-purity indium (6N) solder. A 0.5-μm-thick GaAs buffer layer was first grown at 580°C, then the temperature was decreased to below 510°C for the growth of the $In_{0.5}Ga_{0.5}P$ layer. All $In_{0.5}Ga_{0.5}P$ epilayers in this study were about 0.9 μm thick. The growth rate of $In_{0.5}Ga_{0.5}P$ was held at 0.6 μm/h and the V/III ratio was about 6. Another set of samples was grown under similar growth conditions as those used for the previous samples, but with 10 pairs of $In_xAl_{1-x}P/In_xGa_{1-x}P$ (50 Å/50 Å) SL between the GaAs buffer and the $In_{0.5}Ga_{0.5}P$ epilayer, in order to eliminate the short-term transient of In flux due to radiative cooling of the evaporating surface after opening the In shutter. Although the Ga cell also has some short term flux transient, it is much smaller and can be ignored in our system according to the

*E-mail address: yccheng@gecko.cp.nctu.edu.tw

calibration prior to the growth. All the samples grown in this study were characterized by photoluminescence (PL) and polarized photoluminescence (PPL) methods. Room temperature PL and PPL were measured using a diode-pumped solid state laser (532.8 nm). The composition of the $In_{0.5}Ga_{0.5}P$ layer was determined by double crystal X-ray diffractometry.

3. Results and Discussion

Using the PL peak energy of the $In_{0.5}Ga_{0.5}P$ epilayer grown on the exact (100) GaAs substrate (0° tilting) as the reference, the PL peak energy shift versus the substrate's tilting angle of $In_{0.5}Ga_{0.5}P$ epilayers grown without the SL buffer is shown in Fig. 1. In which the peak energy of $In_{0.5}Ga_{0.5}P$ grown on the (001)A exact GaAs substrate by SSMBE is about 1.886 eV. The data noted for SSMBE were taken from samples grown in this study, and the data noted for GSMBE were taken from samples grown by another group[7] for comparison. All the samples grown on tilted substrates showed a peak energy shifting to the higher energy side with increasing tilting angle. The highest PL peak energy shift was observed from the sample grown on a 15° tilted substrate by SSMBE and was about 17 meV, which is similar to that for the sample grown by GSMBE,[7] but lower than that for the sample grown by MOCVD.[5] The difference in the peak energy shift between the samples grown by MBE and MOCVD is probably due to the different ordering intensity in the reference sample grown on the 0° tilted substrate, where the growth temperature in the case of MOCVD is much higher than that the case of MBE. Therefore, a stronger ordering intensity is expected in the MOCVD grown sample, and the ordering suppression effect when using the tilted substrate is more prominent in the case of using MOCVD than that in the case of using MBE.

The ordering induced bandgap reduction effect was reasoned to be due to the lowering of crystal cubic symmetry which results in the splitting of the heavy hole and light hole bands,[10] and consequently, lowers the bandgap energy of this ordered material. The suppression of spontaneous ordering by the growth on tilted substrates was attributed to the inclusion of growth kinetics at the step edges of tilted substrates in addition to the growth mechanism of surface diffusion in epitaxy. For substrates with lower tilting angles or exact (001) orientation, the density of steps is too low and the terraces are too long such that the Ga atom can bond first with As because of its higher sticking coefficient and bonding energy. Since In has a relatively large atomic diameter compared with that of Ga, there is a barrier for In to enter the group III position in the alloy in addition to the ordinary barrier for entering the kink position from the surface site.[3] Consequently, the formation of natural spontaneous ordering is generated. When the substrate's tilting angle is increased, the height and density of atomic steps are also increased, and now the growth mechanism is determined by the step flow mode.[3] There are three dangling bonds on each step and two dangling bonds on each terrace, therefore, step flow growth results in that all the group III atoms migrate on the terrace and bond at the step. Surface segregation of group III atoms are eliminated because of the stronger bonding energy at the steps. The results shown in Fig. 1 also indicate that, although the degree of ordering phenomena may be different in each of the epitaxial methods due to different growth mechanisms, the spontaneous ordering effect exists in all InGaP samples grown by SSMBE, GSMBE and MOCVD even with tilted substrates.

As mentioned previously, the ordering effect is initiated at the beginning of epitaxial growth by the surface strain due to the different atomic sizes and bonding energies. Therefore, the ordering effect is expected to be reduced by eliminating the initial surface strain. Since the interfacial strain can be eliminated by using a SL buffer layer,[8] the PL peak energy versus substrate's tilting angle of samples grown with and without an InAlP/InGaP SL buffer layer are shown in Fig. 2. At the same tilting angle, the energy gap of the $In_{0.5}Ga_{0.5}P$ epilayer with the SL buffer layer is always higher than that without the InAlP/InGaP SL buffer layer. The highest peak energy difference of ~8 meV is observed from the

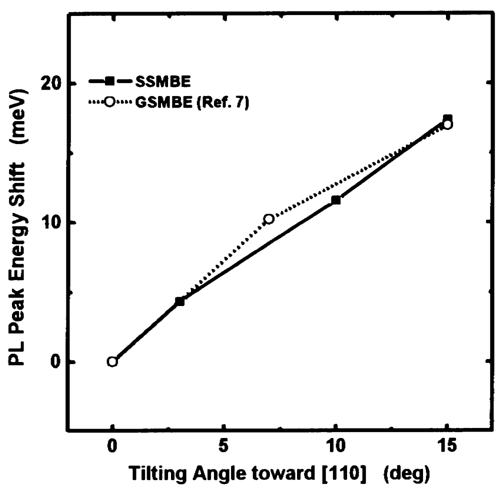

Fig. 1. Room temperature PL peak energy shift versus substrate's tilting angle, the reference of the energy shift is the peak energy of $In_{0.5}Ga_{0.5}P$ grown on a 0° tilted substrate and its peak energy is about 1.886 eV. The solid squares are data measured in this study (SSMBE), the open circles are data taken from ref. 7 (GSMBE).

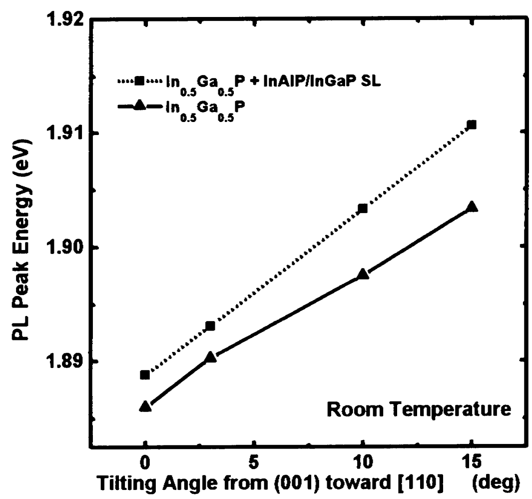

Fig. 2. Room temperature PL peak energy versus substrate's tilting angle. The solid triangles are data taken from the samples grown without the InAlP/InGaP SL buffer, and the solid squares are data taken from the samples grown with the InAlP/InGaP SL buffer.

samples grown on the 15° tilted substrate with and without the InAlP/InGaP SL. The PL peak energy of $In_{0.5}Ga_{0.5}P$ grown on the 15° tilted substrate with SL buffer layers is 1.91 eV, similar to that of fully disordered $In_{0.5}Ga_{0.5}P$ grown by liquid-phase epitaxy.[11)]

Figure 3(a) shows the room temperature polarized PL spectra of an $In_{0.5}Ga_{0.5}P$ sample grown on a 15° tilted substrate with an InAlP/InGaP SL buffer layer, and Fig. 3(b) shows the PPL spectra of $In_{0.5}Ga_{0.5}P$ grown on an exact (001) GaAs substrate without SL buffer. For exciting light linearly polarized along the [110] crystal axis, the PL emission from the sample is referred to as [110] polarization, and is indicated by the solid line. For exciting light linearly polarized along the $[1\bar{1}0]$ crystal axis, the PL emission from the sample is referred to as $[1\bar{1}0]$ polarization, and is indicated by the dotted line. As shown in Fig. 3(a), the difference of peak energies between [110] polarization and $[1\bar{1}0]$ polarization is less than 2 meV, while it is about 27 meV in Fig. 3(b). The polarization behavior can be explained by the competition of emissions associated with the degenerate valence band in the semiconductor. When there is no ordering, only a very small peak energy difference will be observed due to a non-splitting but degenerate valence band. When ordering appears in the epilayers, the degenerate valence band will split into two bands, band A for Γ_{6v} and band B for Γ_{4v}, Γ_{5v}, where band A lies below band B.[12)] Since the luminescence with the $[1\bar{1}0]$ polarization is dominated by transitions related to band B, the peak energy of $[1\bar{1}0]$ polarization is lower than that of [110] polarization, and a larger peak energy difference indicates a stronger ordering effect.[13)] Apparently, the ordering effect in the sample grown on the 15° tilted substrate with SL buffer is much smaller than that in the sample grown on the exact (100) substrate without a SL buffer. It is worth noting that the full-width at half maximum (FWHM) is noticeably reduced in the case of growth with SL and a higher substrate tilting angle. Since all samples in this study were undoped, this FWHM reduction is probably due to the smaller composition fluctuation in the sample with a lower ordering effect.

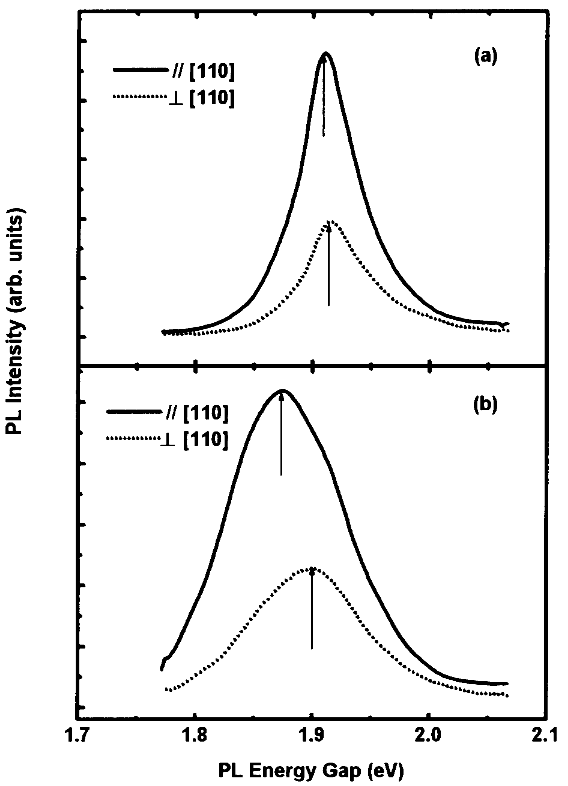

Fig. 3. Polarized PL (PPL) spectra of the $In_{0.5}Ga_{0.5}P$ epilayer (a) grown on a 15° tilted substrate with an InAlP/InGaP SL buffer, (b) grown on a 0° tilted substrate without a SL buffer.

4. Conclusions

We have studied the effect of using a tilted substrate in the growth of $In_{0.5}Ga_{0.5}P$ grown by SSMBE. We found that the PL peak energy shift of $In_{0.5}Ga_{0.5}P$ grown by SSMBE due to substrate tilting is similar to that grown by GSMBE, but different from that grown by MOCVD. However, our results indicate that there is still a weak ordering effect in $In_{0.5}Ga_{0.5}P$ epilayers[6)] grown by SSMBE using a phosphorus-valved cracker, although the ordering intensity may be smaller than that in the epilayers grown by MOCVD. In addition, in order to eliminate the transient In flux after opening the In shutter, we have grown InAlP/InGaP SL buffer layers before the growth of $In_{0.5}Ga_{0.5}P$. We observed that the $In_{0.5}Ga_{0.5}P$ epilayer grown on the 15° tilted substrate with an InAlP/InGaP SL buffer layer showed a peak energy similar to that of a fully disordered sample. Apparently, by growing an $In_{0.5}Ga_{0.5}P$ epilayer on a tilted substrate with a SL buffer layer, the ordering effect is drastically reduced. This reduction of ordering intensity is attributed to the elimination of the initial surface strain by the SL buffer.

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