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Heteroepitaxy of InP on (100)Si by Organometallic Vapor Phase Epitaxy

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Growth of InP on (100)Si substrates has been studied with organometallic vapor phase epitaxy. Single-domain InP films were successfully grown by optimizing substrate preheating procedures. Grown films were characterized using photoluminessence(PL) measurement and pnjunction characteristics. Heteroepitaxial films showed PL intensity as high as one-third of that from homoepitaxial films, and pn-junction formed in heteroepitaxial InP showed a relatively high quantum efficiency in the photoresponse. It was also shown that residual stress in InP/Si was small compared to those in GaAs/Si and GaP/Si, indicating a high reliability for InP/Si systems.

1. Introduction

Heteroepitaxy of III-V semiconductors on Si substrates is a very attractive technology because of its application to opto-electronic integrated circuits¹⁾, thin-film solar cells²⁾ and so forth. However, the major difficulties to obtain high-quality III-V heteroepitaxial films on Si are 1)the formation of antiphase domains(APDs) related to the growth of polar semiconductors on non-polar ones, 2)highdensity dislocations in films due to the lattice mismatch and 3)residual stress in grown films due to the difference of the thermal expansion coefficient between a film and a substrate.

Up to now, many attentions have been concentrated on the heteroepitaxy of GaAs on Si^{1-4} , this system has 4.1% lattice mismatch, and device quality GaAs films have been already obtained. However, there is a few attempts of heteroepitaxy of InP on $\mathrm{Si}^{5,6}$, because of the large lattice mismatch(8.1%) between InP and Si.

In this paper, we report the successful growth of single-crystalline InP thin films on Si by the organometallic vapor phase epitaxy (OMVPE) technique and the characterization of grown films.

2. Experimental

Thin-film InP was grown with the low pressure(~76Torr) OMVPE system⁵). As source materials, triethylindium(TEIn) and phosphine(PH₃, 20% in H₂) were used with a carrier gas of H₂. Substrates of Si (~2x2cm², 500µm-thickness) were (100)-oriented(accuracy of ± 0.5 deg.) and of n-type(~0.02 Ω ·cm). The substrates were degreased, and dipped in a HF solution to remove surface oxides just before loading into the reactor.

The growth of InP thin films were carried out with the two-step growth method. Prior to the growth, the substrates were preheated to $850\sim1030^{\circ}$ C in H₂ in order to desorb native oxides of Si surface. The first-layer(~200 Åthick) was grown at $\sim400^{\circ}$ C with a TEIn/PH₃ ratio ~250 , and annealed at $\sim600^{\circ}$ C for about 5min. Then, the second-layer was grown on the 1-st layer at $\sim600^{\circ}$ C, where the thickness and the growth rate were $\sim5\mu$ m and $\sim3\mu$ m/hr, respectively. For comparison, the ordinary one-step growth was also performed at $\sim600^{\circ}$ C.

3. Results and discussion

3.1 Growth of single-domain InP films

Figure 1 shows the x-ray diffraction pattern from an InP/Si prepared with the twostep growth. The pattern contained 3 peaks of InP(200), InP(400) and Si(400), showing the (100)-oriented InP grown on (100)Si. Figure 2 shows the reflection high energy electron diffraction(RHEED) patterns from the 1-st and 2-nd layers. As shown in Fig 2(a), the 1-st layer showed a defined but spotty pattern. The 2-nd layer, on the other hand, showed a welldefined and streaked pattern with Kikuchi lines, indicating the excellent crystalline quality of the layer. It was found that the crystalline quality of the 1-st layer was markedly improved as the growth rate was decreased. The crystalline quality of the 2-nd layer was dependent on that of the 1-st layer.

Figure 3 shows the surface Nomarskiphotograph of a heteroepitaxial InP film grown with the two-step growth method. One can see that a smooth InP film with a good mirror surface was obtained. Surface morphology of



Fig. 1 X-ray diffraction pattern from InP film grown on (100) Si.



Fig. 2 RHEED patterns from (a) 1-st layer ($\sim 200\text{\AA}$ -thick) and (b) 2-nd layer($\sim 5\mu$ m-thick) of InP grown with two-step growth method.



Fig. 3 Nomarski photograph of InP film (~5µm-thick) grown two-step growth method.

InP grown with the ordinary one-step growth was inferior to that of the two-step grown InP. This fact suggests that island growth of InP at the early stage of growth was suppressed by covering the substrate surface with a low-temperature (~400°C) grown film.

In order to prepare a device quality InP films on Si, the formation of APDs should be suppressed because APDs act as majority carrier scattering and/or minority recombination centers. The effect of the preheating temperature on the suppression of APDs was studied. To reveal the domain structure of InP films, the films were chemically etched with a H2SO4+H2O2+H2O solution, which makes etch pits aligned to <011> direction. Figure 4 shows the etched pattern of InP films grown on Si with an and 1030°C-preheating before growth. 850° C-The etched pattern for the 850°C preheating showed an APD structure, in which small regions having etch pits aligned to two different direction, i.e., <011> and <011>, were contained. On the other hand, the pattern



Fig. 4 Nomarski photograph of etched InP films (~5µm-thick) grown after (a) 850°Cand (b) 1030°C-preheating.

for the 1030° C-preheating showed a singledomain structure with etch pits aligned to $<0\overline{1}1>$ direction.

For a preheating temperature in the range $950 \sim 1030^{\circ}$ C, single-domain InP films were reproducibly obtained. This result seems to show that, in this temperature range, Si surface oxides were sufficiently removed and/or bi-atomic layer steps are formed on the Si substrate⁷. Thus, it was clarified that the preheating temperature is the dominant factor in obtaining single-domain InP films on Si.

The density of dislocations estimated from etch-pit density in Fig.4 was about $5 \times 10^7 \text{ cm}^{-2}$ in 5µm-thick InP. The reduction of the dislocation density is essential to obtain high quality InP films on Si.

3.2 Electrical and optical properties of heteroepitaxial InP films

Photoluminessence(PL) spectra from grown InP films were measured at 77K with an Ar-ion laser(5145Å). Figure 5 shows the PL spectra for hetero- and homo-epitaxial InP films, both were grown with the same condition. In the measured wavelength ($850 \sim 1000$ nm), PL spectra of both films consisted of a single peak at ~ 880 nm. The PL-intensity from the



Fig. 5 PL spectra of hetero- and homoepitaxial InP films(~5µm-thick).

heteroepitaxial InP film was about one-third of that from the homoepitaxial one. The relatively low PL intensity for the heteroepitaxial films may be due to the highdensity dislocation. The peak energy for the heteroepitaxial InP film was lower by about 6.4meV than that of homoepitaxial films. This shift is due to the residual tensile stress in heteroepitaxial InP films, as discussed in the next section.

In order to clarify the quality of heteroepitaxial InP films, a pn-junction was formed in InP films and its photoresponse was measured. The p- and n-layers were Zn-doped ($\sim 10^{17} \text{ cm}^{-3}$) and non-doped($\sim 10^{16} \text{ cm}^{-3}$), respectively. The junction depth and the total layer thickness were 0.5µm and 5µm, respectively. The junction area was $\sim 5 \times 5 \text{ mm}^2$.

Figure 6 shows current-voltage characteristics of a fabricated pn-junction. The junction showed typical rectification characteristics though a relatively large leak-current in the reverse bias was observed. The junction showed a low built-in voltage (~0.4V). Figure 6 also shows the good photoresponse of the illuminated(100mW/cm^2) junction. Figure 7 shows a spectral response of the junction. The response was very similar to that for a junction formed in a homoepitaxial films though the quantum efficiency is about $1/2 \sim 2/3$ of that for the



Fig. 6 Current-voltage characteristics of a pn-junction formed in heteroepitaxial InP film.



Fig. 7 Spectral response of a pn-junction formed in a hetero- and homo-epitaxial InP films.

homoepitaxial junction. In order to obtain the quantum efficiency equal to that of the homoepitaxial junction, it is necessary to reduce the dislocation density to $<10^{6}$ cm⁻².

3.3 Residual stress in InP films

The residual stress in InP films grown on (100)Si was estimated from the PL peak-energy shift⁵⁾ and the curvature of the InP/Si system. Figure 8 shows the comparison of the residual stress estimated from the curvatures for InP/Si, GaAs/Si and GaP/Si. It can be seen that the residual stress in InP/Si was the smallest in the three systems. For these systems, the stresses estimated from the PLshift were larger than those from the curvature. The low stress in InP films is due to the small discrepancy of the thermal



Fig. 8 Comparison of residual stress in InP, GaAs and GaP films grown on Si substrates. Residual stress was estimated from curvatures of film/substrate systems.

expansion coefficient between Si and InP, and the low growth temperature of InP. This result is supported by the fact that no cracks were found in 10µm-thick InP films, while cracks were observed in GaAs films of >3µm-thick⁴⁾. For devices using heteroepitaxial InP films, low residual stress will lead to the high reliability of the devices.

6. Conclusion

The OMVPE growth and characterization of films on Si substrates have been TnP reported. Single-domain InP films were grown by optimizing substrate preheating procedure. Heteroepitaxial InP films with relatively good electrical and optical properties were obtained in the early stage of the study, because PL intensity from the films was about one-third of that from homoepitaxial ones and a pn-junction showed good photoresponse. Studies will be make on applications of heteroepitaxial InP films, for example, thinfilm solar cells, InGaAsP/InP DH lasers and so forth. For these applications, it is the most important to reduce dislocations in InP films. Acknowledgments

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