LOW SUPERSATURATION OVERGROWTH OF NANOPOROUS GaAs SUBSTRATES

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Abstract

Oriented pore networks in GaAs substrates were created by electrochemical dissolution. Pore etching duration in the range of 0.5 to 450 s was used. The porous substrates were treated for 16 – 24 hours at 250 – 350 °C in high vacuum and ultra pure hydrogen. Low supersaturation overgrowth of the porous substrates by In$_x$Ga$_{1-x}$As ($x$<4%) was realized by Liquid Phase Epitaxy (LPE). Shorter pore etching time resulted in better epitaxial layer morphology. The influence of the melt supersaturation on the properties of the overgrown strained layer is discussed in detail. The maximum In content at which the layer shows good quality was increased from 2.8% for a conventional substrate to 3.4% on a porous substrate.

Kye words: Porous III-V semiconductors, Electrochemical etching, Pore conversion, Heteroepitaxial growth.

1. INTRODUCTION

Traditional semiconductor epitaxial growth using planar monolithic substrates has progressed from homoepitaxy to lattice-matched heteroepitaxy and recently to pseudomorphic, lattice mismatched systems where small amounts of strain are accommodated in very thin films. When utilization of the heterointerface is not required, one is willing to tolerate various intermediate layers, so long as the top working layers are of desired device quality. Original theory of Luryi and Suhir [1] demonstrates the possibility of the dislocation density decreasing when Si$_{1-x}$Ge$_x$ on porous Si is grown. This approach has been reformulated as the theory
of nanoheteroepitaxy in [2], which predicts for nano-island radii in the 10 nm to 100 nm range that it is possible to eliminate mismatch defects for heteroepitaxial layers, that are mismatched as much as 4.2%.

**Fig. 2.** Pore depth dependence on anodisation duration in the HF-H₂O-KI solution.

**Fig. 3.** Pores anodised in GaAs by HF-H₂O-KI electrolyte.
2. RESULTS AND DISCUSSION

Different electrolytes for pore etching in GaAs were tested. The best results were observed with the electrolyte containing diluted HF and KI. This electrolyte was originally used in Ref.[3]. Porous etching rate in GaAs \([N_D-N_A] \approx 9 \times 10^{17}-3 \times 10^{18} \text{cm}^{-3}\) is demonstrated in Fig. 2. and the SEM cross-sectional image of the porous substrate is in Fig. 3. The porous GaAs as well as InP layer retained single-crystalline structure of the initial monolithic substrate and had a mirror-smooth or pierced surfaces suited for epitaxial growth. Extensive description of our experimental results was published in [4-6]. Simultaneous epitaxial overgrowth of the porous and nonporous GaAs substrates by Liquid Phase Epitaxy (LPE) from the Ga-In-As melt supersaturated in range 1 to 13 °C were realised. The growth took place in the supercooling regime with a cooling rate 0.2–0.4 °C/min. The epitaxial layers were simultaneously grown on GaAs (100) substrates with two different depths of pores and one monolithic substrate without pores. The growth temperature was 690 °C. The growth on monolithic and shallow-pore substrates at low supersaturations (~1 °C) resulted in the identically [1-10] oriented lamellar surface morphology while in the deep-pore substrates (etching time 150 s), the dominant lamellar or rippled orientation partially disappeared.

![Fig. 4. Surface morphology of the In\(_x\)Ga\(_{1-x}\)As (x= 0.02) layers grown simultaneously on a monolithic, shallow-pore (etched for 0.4 s), and deep-pore substrate (etched for 150 s). The melt supersaturation corresponds to \(\Delta T \sim 1^\circ\text{C}\).](image)

At low supersaturation, the low surface diffusion rate in [110] direction dominates and the surface morphology of the layers grown on monolithic GaAs substrates and shallow and deep–pore substrates is similar, see Fig. 4. The significant improvement in deposited InGaAs layers has been observed when the melt supersaturation increases. In our experiments, the value of supersaturation corresponding to \(\Delta T\) in the range 1 to 13 °C was tested. At values higher than 10 °C a spontaneous crystalisation in the melt was observed. Finally the \(\Delta T \sim 8.5 – 9^\circ\text{C}\) was selected as optimal, see Fig. 5. In Fig 5. a/ a cross–hatch pattern, which appears on surface of GaInAs epitaxial layers, dominates. The origin of this structure corresponds to
the misfit dislocations array aligned along [110] and [1-10] directions. Cross-hatching as an evidence of the regular misfit dislocation array could be produced partially during the growth at so high temperature as 690°C and during heat treatment in cooling of the growth crucible. Generally, heterostructures with cross hatching are assumed to have better quality than the same structures without ordered misfit dislocation networks. Simultaneous deposition of In$_x$Ga$_{1-x}$As ($x=1-2.5\%$) on monolithic and porous GaAs substrates demonstrates systematic increase of the layer thickness grown on porous substrates of 15-30 %. This difference roughly corresponds to the work of authors [3]. We suppose that this result is given by the porous-substrate compliance and better strain accommodation within the pores.

Fig. 5. Surface morphology of the In$_x$Ga$_{1-x}$As ($x=0.028$) layer grown on a porous (60 s) GaAs substrate (a/) and In$_x$Ga$_{1-x}$As ($x=0.035$) on a porous (100 s) GaAs substrate (b/). The supersaturation corresponds to $\Delta T \sim 8.5^\circ$C. The melt composition was different.

The photoluminescence spectra shown in Fig. 6. reveal a change in the band-gap of the In$_x$Ga$_{1-x}$As solid-solution layer grown on monolithic substrate of the order of 30 meV with respect to the PL maximum of the GaAs substrate. Further, the maxima of the PL-spectra grown on porous substrates generated at 60 and 100 s pore formation process are shifted by further 6 meV toward lower energies, which implies higher In content in this solid solutions compared to the layer grown on a conventional substrate. These values can be considered as correct, provided the doping level in all studied layers remains constant, i.e. one need not to consider band-gap shrinkage caused by an increased doping level. Assuming that for small In contents we can neglect the bowing in the Wegard’s dependence of this solid solution, we evaluate the In-content in the layer grown on a conventional substrate as $x=2.84\%$, while for the layers grown on porous substrates we obtain $x=3.4\%$, respectively. It should be mentioned that the different duration of the pore formation does not bring measurable change in the In content. The In-content in the layers grown on conventional substrates depends obviously on the epitaxial growth conditions such as the melt composition and its supercooling.
3. CONCLUSION

Comparison of the substrates with different pore depths gives different results depending on melt supersaturation. At low supersaturation (1 to 2 °C) and deep pores the growth morphology has been poor. At optimal supersaturation (8 to 9 °C at 690 °C), the surface morphology was very good for both, deep and shallow pores. Optical properties of the simultaneously grown In$_x$Ga$_{1-x}$As layers on porous and monolithic substrates demonstrate better strain accommodation in the case of porous substrates, which potentially improves the reliability of the heterostructure devices. Typical surface morphology is a cross-hatch pattern with ordered misfit dislocation network. Obtained indium content during LPE with melt supersaturation 8 to 9 °C approaches to 4 %. Higher lattice mismatch can be obtained by metal organic vapour phase epitaxy (MOVPE) [6,8,9] or other nonequilibrium techniques.

ACKNOWLEDGMENT

The work was supported by the project P108/10/0253 of the Czech Science Foundation.
REFERENCES


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