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ABSTRACT

The objective of this work is to perform transmission electron microscopy (TEM) studies of GaP(N,As) alloys grown by metal-organic chemical vapor deposition (MOCVD) on Si substrates. These alloys are of interest for the fabrication of high-efficiency tandem solar cells based on Si. The results indicated that the nucleation and growth conditions used are critical for obtaining planar epitaxial layers with a low defect density. In particular, antiphase domains are eliminated using a low growth temperature. TEM studies of these alloy layers, which contain only a few percent N, revealed no phase separation. However, electron diffraction studies revealed the first evidence of CuPt-type atomic ordering in these P-rich, dilute nitride alloy layers.

1. Objectives

The objective of this research is to study, using transmission electron microscopy (TEM), epitaxial layers of GaP(N,As) alloys grown by metal-organic chemical vapor deposition (MOCVD) on Si substrates. These alloys are being investigated for application in III-V/Si lattice-matched tandem solar cells that have potential efficiencies greater than that achievable by current Si-based technology [1, 2]. The aim of this work is to determine the nature and origin of defects introduced during nucleation and growth of the layers to aid optimization of growth procedures and eliminate defect generation. The compositional uniformity of the alloy layers is also investigated.

2. Technical Approach

GaP(N,As) alloys can be grown lattice-matched on Si substrates, offering the potential to achieve much reduced defect density layers in comparison to lattice-mismatched systems such as GaAs/Si. In addition, a lattice-matched alloy can be grown with a direct bandgap that is near the optimum to produce the highest predicted efficiency for an III-V/Si tandem solar cell [1, 2]. Despite the close lattice-match to Si, growth of these III-V alloys with high structural and optical quality is challenging for several reasons. Clean, oxide-free, planar Si surfaces are required prior to growth to avoid nucleation problems and the introduction of antiphase domains (APDs) at the III-V/Si interface. The growth conditions during nucleation are also critical to avoid the formation of three-dimensional islands that can result in the generation of stacking faults and threading dislocations as the islands coalesce. Mismatch of thermal expansion coefficients can also result in the cracking of layers. In addition, GaP(N,As) alloys are expected to become unstable toward phase separation as more N is added, and differences in the atomic sizes of the group V atoms may drive the alloy to atomically order during epitaxial growth. We have therefore performed TEM studies on thin cross-section and plan-view specimens of these alloy layers, prepared using standard techniques, in a Philips CM30 operated at 300 kV.

3. Results and Accomplishments

All the samples examined in this work were grown by MOCVD in a reduced pressure (200 torr) reactor on (001) Si substrates offcut by 2˚ toward (111). Prior to growth of alloy layers on Si substrates, a thin (~ 40 nm) GaP nucleation/buffer layer was grown.

Non-optimized nucleation and growth conditions for the GaP buffer layer and non-optimized Si substrate preparation resulted in island growth and the generation of a high density of threading dislocations and APDs in the layers. The best Si substrate preparation was found to be a cleaning in 2:1:10 (ammonia: H_2O_2: H_2O) solution followed by etching in HF. In the reactor, the substrate was heated up under H_2 and then annealed under a low flow of AsH_3 for 10 minutes at 800˚C prior to growth of the GaP buffer layer. The growth temperature of the GaP buffer was found to be a key parameter in obtaining planar growth, eliminating APDs, and reducing threading dislocation density. Fig. one shows a plan-view TEM micrograph of a thin (60 nm) GaP nucleation layer deposited on a Si substrate at 850˚C. GaP layers deposited under these conditions contained a high density of APDs (see Fig. 1). The APDs were eliminated by initiating growth of the GaP nucleation/buffer layer at the

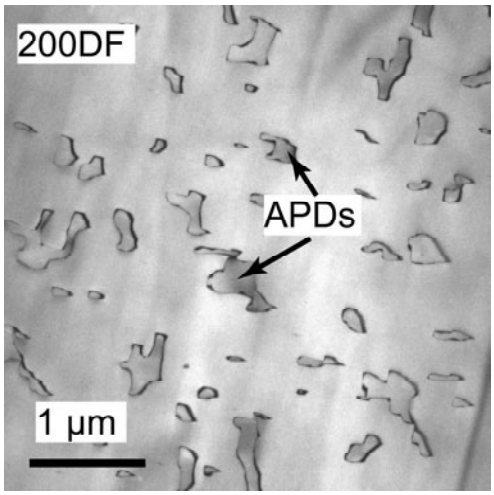

Fig. 1. Plan-view TEM micrograph of GaP buffer layer grown on Si substrate at 850˚C containing a high density of APDs.

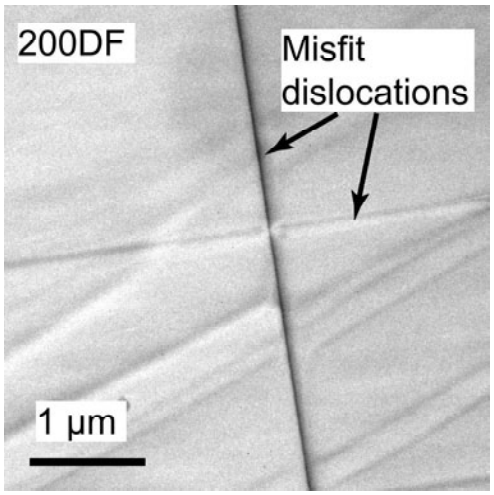

Fig. 2. Plan-view TEM micrograph of GaP buffer layer grown on Si substrate initially at 800˚C.

lower temperature of 800˚C (see Fig. 2), with the temperature subsequently increased during growth to 850˚C over several minutes. The only defects observed in such layers were a low density of interfacial dislocations associated with the lattice misfit between the GaP and the Si substrate. APDs can originate at certain types of atomic steps at the III-V/Si interface [4]. A long surface diffusion length at higher growth temperatures can enhance the growth of APDs [4].

Using GaP buffer layers nucleated under these conditions, we have achieved growth of planar GaP(N,As) alloy layers with no detectable APDs and a significantly reduced threading dislocation density, e.g., see Fig. 1 in [3].

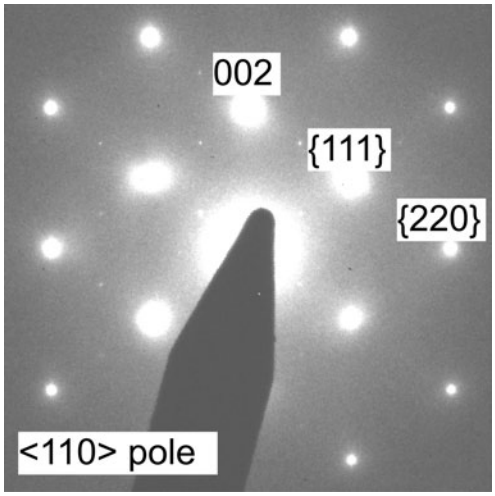

Fig. 3. (110) TED pattern showing evidence of CuPt-type atomic ordering in a $GaN_{0.98}P_{0.02}$ alloy layer grown at 600˚C.

TEM studies of all the GaNPAs and GaNP alloy layers, containing only a few percent N, examined so far revealed no evidence for phase separation. However, transmission electron diffraction (TED) studies of these GaNPAs and GaNP alloy layers grown in both a reduced pressure (200 torr) and an atmospheric pressure MOCVD reactor have revealed the first evidence of CuPt-type atomic ordering on {111} planes in these P-rich, dilute nitride alloys, e.g., see Fig. 3. This ordering is believed to be associated with anion-anion dimerization resulting from reconstruction of the (001) surface that occurs during epitaxial growth. The ordering is driven by strain associated with incorporating the different-sized group V atoms at the reconstructed growth surface. The occurrence of atomic ordering in these alloy layers is significant because it can have important effects on the optical and electronic properties of the alloys. The dimer-induced mechanism of atomic ordering has also been predicted to enhance the solubility of N near the surface in III-V semiconductors [5]. Subsequently, this high concentration of N may remain frozen in during further layer growth depending on the growth conditions used.

4. Conclusions

We have performed TEM studies to investigate the nature and origin of defects generated during the MOCVD growth of GaP(N,As) alloys on Si substrates. The results demonstrated that the nucleation and growth conditions used are key in obtaining low defect density layers. We have found no evidence of phase separation in the alloys examined, which only contained a few percent N. TED studies revealed the first evidence of CuPt-type atomic ordering in these P-rich, dilute nitride alloys. This ordering could have significant effects on the optical and electronic properties of the layers and also enable a higher solubility of N in the material. Future work will concentrate on further study of defect generation and the occurrence of atomic ordering during growth of this material, with the aim of greater improvements in the layer quality.

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15. SUBJECT TERMS
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