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Structural Studies of 1-eV Solar Cell Materials Lattice-Matched to GaAs

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ABSTRACT

Structural studies using transmission electron microscopy have been made on 1-eV band-gap materials, lattice-matched to GaAs and Ge substrates, grown by metal-organic vapor-phase epitaxy for use in multijunction, high-efficiency solar cells. $(GaAs)_{1-x}(Ge_2)_x$ alloy layers exhibited pronounced phase separation during epitaxial growth. $Ga_{1-x}In_xN_yAs_{1-y}$ layers grown under a wide range of conditions, using both hydrazine and dimethylhydrazine as nitrogen sources, have also been investigated. Layers grown at high temperatures (650˚C) using dimethylhydrazine contained a high density of "comet"-like precipitates that are associated with a high concentration of carbon and hydrogen, as revealed by secondary ion mass spectrometry. GaN_yAs_{1-y} layers grown with hydrazine at 550˚C were observed to undergo a transformation from single-crystal epitaxial layers at low hydrazine/III flow ratios to nanocrystalline or amorphous layers at high hydrazine/III flow ratios.

1. Introduction

By inserting a 1-eV junction between the GaAs and Ge junctions of the current state-of-the-art high-efficiency GaInP/GaAs/Ge cascade solar cell, it is predicted that the overall efficiency of the device may be significantly improved [1]. Several 1-eV band-gap materials, such as $(GaAs)_{1-x}(Ge_2)_x$ and $Ga_{1-x}In_xN_yAs_{1-y}$ alloys, lattice-matched to GaAs and Ge substrates to maintain high crystalline quality, are being investigated for incorporation into these multijunction solar cells. Structural studies of these materials have been performed using transmission electron microscopy (TEM) and diffraction (TED).

2. Results

2.1 $(GaAs)_{1-x}(Ge_2)_x$

Although GaAs and Ge are size-matched, they are mutually insoluble in the equilibrium bulk state, leading to almost complete phase separation into GaAs- and Ge-rich regions at all temperatures below the melting point. Despite this strong tendency toward phase separation, relatively homogeneous epitaxial $(GaAs)_{1-x}(Ge_2)_x$ alloy layers have been reported, grown by non-equilibrium techniques such as metal-organic vapor-phase epitaxy (MOVPE), sputter deposition, and molecular-beam epitaxy (MBE). In this work, $(GaAs)_{1-x}(Ge_2)_x$ alloy layers were grown by MOVPE under a wide range of growth conditions using trimethyl gallium, arsine, and germane as source materials. All the layers grown with these source materials exhibited pronounced phase separation into regions of GaAs-rich zinc-blende material and Ge-rich diamond cubic material [2,3]. Fig. 1 shows a 002 dark-field (DF), chemically sensitive, (110) cross-section TEM micrograph of a $(GaAs)_{0.90}(Ge_2)_{0.10}$ layer grown at 640˚C. The phase-separated microstructure in this layer is remarkably regular, with thin sheets of Ge-rich material lying on both sets of {115}B planes and is associated with a faceting of the growth surface on these planes [2,3]. In some areas, the Ge-rich material is in the form of closely spaced clusters or rods lying on {115}B planes. As the growth temperature was increased to 690˚C, the phase-separated microstructure evolved into large, irregular-shaped Ge-rich plates lying roughly parallel to the (001) plane in a GaAs-rich matrix [3]. Growth on a {115}B orientation substrate resulted in the spontaneous formation of a GaAs-rich/Ge-rich superlattice along the [115]B growth direction [3]. The occurrence of this phase separation was associated with substantial band-gap narrowing. Recent results have suggested that we may be able to kinetically suppress the phase separation by growth at low temperatures and high growth rates.

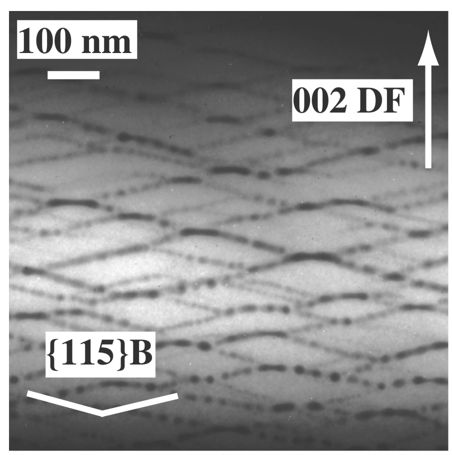

Fig. 1. (110) cross-section, 002 DF TEM image showing phase-separated microstructure of $(GaAs)_{0.90}(Ge_2)_{0.10}$ layer grown at 640˚C.

2.2 $Ga_{1-x}In_xN_yAs_{1-y}$

$Ga_{1-x}In_xN_yAs_{1-y}$ can be grown lattice-matched to GaAs or Ge substrates with a band gap of ≈ 1 eV for x ≈ 3y and a N content of about 2% [4]. MOVPE growth of the above 1-eV band-gap alloy has been performed using dimethylhydrazine (DMHy) as a nitrogen source at growth temperatures of 580˚ and 650˚C. However, the grown layers typically exhibit low minority-carrier diffusion lengths, high junction recombination, and a high p-type background doping concentration, which are serious problems for their application in solar cells [5]. The reason for these poor electrical properties is not well understood, but may be due to spatially localized band fluctuations associated with the presence of isolated clusters of GaN in the alloy, possibly as a result of the large miscibility gap predicted for this alloy.

TEM studies of layers grown at 580˚C revealed the alloy to be of good structural quality, with a low defect density and no detectable sign of significant N clustering. In layers grown at 650˚C, however, a region of pronounced strain contrast was visible in the lower part of the layers, suggesting that phase separation had occurred, as shown in Fig. 2. More detailed examination revealed this strain contrast to be associated with a band of precipitates lying at the top of the region of strain contrast. These "comet"-like precipitates appeared to have left behind a tail of material of different composition during layer growth, hence resulting in the band of strain contrast observed in the layer below the precipitates. A high density of threading dislocations ($\approx 10^8$ cm^{-2}) was nucleated at this band of precipitates. The position of the band of precipitates correlated with the presence of broad spikes in the hydrogen and carbon contents in the layers, as revealed by SIMS depth profiles. This suggests that the precipitates may be related to hydrocarbon contamination or a gas-phase reaction occurring at high growth temperatures. Similar precipitates were also observed in GaN_yAs_{1-y} layers grown at 650˚C.

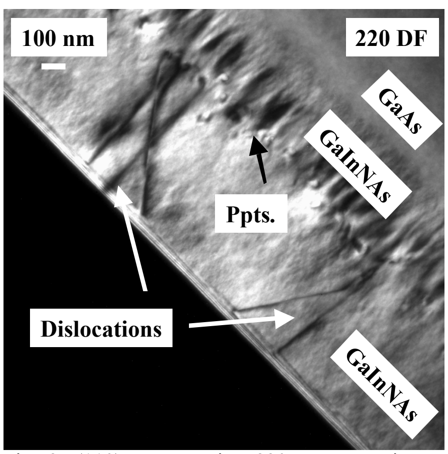

Fig. 2. (110) cross-section 220 DF TEM image showing "comet"-like precipitates (ppts.) and associated band of strain contrast and dislocations in $Ga_{1-x}In_xN_yAs_{1-y}$ layer grown at 650˚C.

Alternative nitrogen sources to DMHy, e.g., hydrazine (Hy), are also being investigated for the growth of these alloys. This is to enable growth at higher temperatures and arsine flows which is expected to lead to an improvement in the minority-carrier properties of the alloy layers [6]. A reduction in the background carrier concentration of the semiconductor alloy was also desired [6].

With Hy, significant N incorporation was obtained at much lower nitrogen source/III flow ratios than would be required using DMHy, although no improvement in background carrier concentration has so far been observed [6]. GaN_yAs_{1-y} layers were grown using AsH_3/III flow ratios of 4.4 and 44, with the Hy/III flow ratio varied over several orders of magnitude at both of these values [6]. At each AsH_3/III flow ratio, layers grown with a Hy/III flow ratio below a critical value were single-crystal epitaxial layers containing a few percent N with well-defined band gaps. Above the critical Hy/III flow ratio at each AsH_3/III flow ratio, the GaN_yAs_{1-y} layers became nanocrystalline or amorphous [6], as shown in Fig. 3, and contained a high N content.

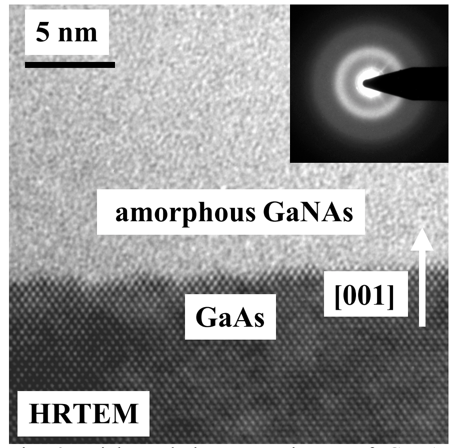

Fig. 3. High-resolution TEM image of GaNAs layer grown at 550˚C with AsH_3/III = 4.4 and Hy/III = 8.6. Inset is TED pattern from GaNAs layer showing that it is amorphous.

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