Comparison studies on growth modes of MBE grown ZnSe on GaAs (111) A and GaAs (111) B, using RHEED

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Abstract - In the last three decades, research into wide bandgap II-VI semiconductors was mainly concentrated on the growth and characterisation of ZnSe based structures on GaAs (001) substrates. Therefore, very little is known about the growth processes on {111} GaAs surfaces. This paper presents the comparison of surface processes during MBE hetero-epitaxial growth of ZnSe epilayer on GaAs (111) A, and GaAs (111) B substrates using reflection high-energy diffraction (RHEED).

A. Introduction

GaAs as a zinc-blende-structured semiconductor has polar surfaces {001} and {111}. Normal to the (001) surface all monolayers are bound by two chemical bonds per atom to their nearest neighbours, while normal to the (111) surface, bonds formed between the two successive monolayers are not equivalent. The unreconstructed {111} surface has one dangling bond per atom. Therefore, different growth modes can be expected for the homoepitaxy growth of the ZnSe epilayer on the (001) and the {111} surfaces of GaAs [1]. In this paper, studies of the growth processes of the ZnSe/GaAs {111} system using real time RHEED investigation are compared.

GaAs (111) surfaces consist of bi-layers of alternately layers Ga and As atoms. Therefore, an unreconstructed (1 x 1) surface of GaAs (111) can consist of a layer of either Ga or As atoms, being denoted as (111) A (Ga-terminated) and (111) B (As-terminated), respectively. Both surfaces have a variety of surface reconstructions. Theoretical and experimental studies of GaAs (111) A and GaAs (111) B surfaces revealed that they reconstructed in different ways. The (111) A surface exhibits only a (2 x 2) reconstruction with two distinct phases [2], [3], while (111) B reconstruction depends upon the surface preparation. It has been found that a GaAs (111) B surface exhibits many different reconstructions [19], such as (2 x 2), (3 x 3), (√3 x √3), (√19 x √19). It also possesses low temperature and high temperature (1 x 1) reconstructions.

B. Experimental methods and results

ZnSe epilayers were grown on epi-ready semi-insulating GaAs (111) A and (111) B substrates, which were oriented to better than 0.1 degree. GaAs (111) B substrates were degreased and chemically etched ex situ before transferring them to the MBE chamber. The native oxide was removed from the substrate surface at 400°C - 450°C by exposing to the atomic hydrogen flux. In order to avoid etch pit creation, the GaAs (111) A substrates were only degreased ex situ, and cleaned insitu using atomic hydrogen flux at a substrate temperature of 450°C. Following the cleaning process, a sharp (1 x 1) RHEED pattern for
GaAs (111) B substrate indicating an As-stabilized surface, and a weak \((2 \times 2)\) for GaAs (111) A has been observed.

**B.1 GaAs (111) A**

ZnSe epilayers on GaAs (111) A at 350°C substrate temperature under Se/Zn atomic flux ratio in the range of \((0.22 - 2.45) \pm 0.05\) have been grown. The qualitative study of the RHEED patterns revealed that after deposition of first few monolayers of ZnSe, subsequent layer-by-layer growth mode was unfavourable and three-dimensional islands were formed on top of this intermediate two-dimensional layer. This indicates a change in the growth mode from a two-dimensional growth mode to a three-dimensional growth mode. The transition time of the change in the growth mode for each sample is also given in [4]. Figure 1 (A) - (D) shows evolution of the RHEED pattern from a 2-D growth mode to a 3-D growth mode in [\(\overline{1}10\)] azimuth for growth ZnSe on a GaAs (111) A. Figure 1 (A) shows the RHEED pattern taken from the substrate. The “cigar shape” diffraction pattern of the major rods indicates a slightly roughened surface. Figure 2 (B) and (C) exhibit a smooth 2-D RHEED \((1 \times 1)\) and \((2 \times 2)\) pattern respectively. The \((1 \times 1)\) surface reconstruction immediately after growth commencement has also been observed for the other samples pattern. This reconstruction lasted for 20-45 seconds depending on growth rate. Finally, figure 1 (D) shows the initial stage of a rough 3-D RHEED pattern. Note the time scale, which is indicated at the bottom of right corner in the RHEED images. The growth started at 20:41:00.

![Figure 1: Evolution of the RHEED pattern of GaAs (111) A substrate (A), 23 seconds growth of ZnSe (B), 68 seconds growth of ZnSe (C), 247 seconds growth of ZnSe (D)]

**B.2 GaAs (111).B**

ZnSe epilayers were grown at a constant substrate temperature of 300°C, and 350°C under various Se to Zn atomic flux ratios in the range of \(0.2 \pm 0.05\) to \(1.25 \pm 0.05\). The beam equivalent pressure (BEP) of Se and Zn was measured using an ionisation gauge, which was placed at the substrate position. The BEP ratio of the elements was converted to the atomic flux ratio using calibrations previously established [5].
Figure 2 (A) shows RHEED patterns from the GaAs (111) B substrate along the [10\overline{1}] and [11\overline{2}] azimuths. The substrate pattern shows sharp streaks perpendicular to the shadow edge, indicating a flat surface with a low temperature (1 x 1) reconstruction. This substrate has been exposed to Zn flux for 60 seconds. Then the ZnSe epilayer was grown for 220 seconds on this substrate at a substrate temperature of 350°C under a relatively high Se/Zn atomic flux ratio of 1.2 ± 0.05. The growth process was interrupted and the Se/Zn atomic flux ratio was adjusted to 0.8, 0.5, and 0.25 by decreasing the Se-cell temperature. The ZnSe film was grown for 240-300 seconds under each above-mentioned Se/Zn atomic flux ratios, at the same constant substrate temperature of 350°C followed by an interruption for 30 to 45 minutes between each growth run, to allow the Se-cell to reach thermal equilibrium. The RHEED pattern started to change during the growth under a Se/Zn atomic flux ratio of 0.8 ± 0.05. This change was more significant under relatively lower atomic flux ratios. Figure 2 (B) shows RHEED patterns of ZnSe epilayer grown under 0.25 ± 0.05. The spotty pattern and broken lines have been observed along, [10\overline{1}], and [11\overline{2}] azimuths respectively. The spotty diffraction indicates a three-dimensional growth mode and a rough surface. RHEED patterns taken along other azimuths, while the sample was rotating, confirmed the growth of ordered three-dimensional structures (mounds) on the surface, which will be discussed later in detail in the next section.

The original high Se/Zn atomic flux ratio was then re-established and the ZnSe epilayer were grown for 300 seconds, the spotty RHEED pattern changed to a rather streaky pattern. This evolution in RHEED pattern indicates a surface morphology transition from an extremely rough surface to a smoother surface. Figure 2 (C) shows a RHEED pattern taken from the same sample grown under a Se/Zn atomic flux ratio of 1.2 ± 0.05. A similar experiment has been repeated for another sample with a substrate temperature of 300°C, and same surface morphologies for low Se/Zn and high Se/Zn atomic flux ratios were observed. The result of these experiments has shown that the surface morphology of ZnSe on GaAs (111) B depends directly upon the Se/Zn flux ratio and hence on the number of Se atoms in the physisorbed state.

Figure 2: RHEED patterns along [11\overline{2}] and [10\overline{1}] azimuths showing surface evolution of ZnSe during the growth on a GaAs (111) B, due to the change of Se/Zn atomic flux ratio. (A): GaAs (111) B substrate at 350°C, (B): After depositing ZnSe epilayer under low Se/Zn ratio 0.25 ± 0.05 at 350°C, (C): After depositing ZnSe film under high Se/Zn 1.2 ± 0.05 at 350°C.
C. Conclusion

ZnSe epilayers on GaAs (111) A at 350°C substrate temperature under Se/Zn atomic flux ratio in the range of (0.22 – 2.45) ± 0.05 have been grown. RHEED pattern studies have shown that the initial growth process starts in a 2-D growth mode and then proceeds in a 3-D growth mode irrespective of the Se/Zn flux ratio. The transition time of the growth mode depends directly upon the Se/Zn atomic flux ratio and subsequently to the growth rate. We consider that the reason for the change of growth mode involves faceting due to the difference between the surface energy of ZnSe (111) A and GaAs (111) A [4].

We have identified two distinct 3-D growth modes of the ZnSe on the GaAs (111) B surface. A rough surface morphology was observed for Se/Zn atomic flux ratio higher than 1.00 ± 0.05 at substrate temperatures of 300°C and 350°C. Creation of ZnSe mounds was observed at substrate temperatures of 300°C and 350°C under Se/Zn atomic flux ratio less than 1.00 ± 0.05.

Creation of ZnSe mounds has also been observed for substrate temperatures higher than 400°C under Se/Zn atomic flux ratio in the range of 1.70-5.00 ± 0.05, while a rough surface morphology with no mounds was achieved for substrate temperature less than 400°C under the same Se/Zn atomic flux ratio region. A model has been presented to explain these surface morphologies, which is based on the step-edge barrier [5].

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References