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Formation and characterization of GaAs/As superlattice grown by molecular beam epitaxy at low substrate temperature

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Abstract

High-resolution X-ray diffractometer and transmission electron microscope (TEM) are used to characterize the redistribution of As precipitates in Si δ-doped GaAs grown by molecular beam epitaxy at low substrate temperature (230°C). The superlattice satellite peaks are observed for samples annealed at 700–800°C for 10 min, which is attributed to the formation of a GaAs/As superlattice during the annealing period. The degree of As precipitates confined on the δ-doped planes is revealed on the intensity of satellite peaks in the X-ray rocking curves, as confirmed by the TEM observations. The lattice expansion and contraction of the annealed low-temperature epitaxial layers can be easily observed from the asymmetry of the satellite peaks.

1. Introduction

GaAs grown by molecular beam epitaxy (MBE) at low substrate temperature (LT) has recently received much attention, due to its unique electronic and optical properties [1–6]. When grown at ~200°C, the LT materials are very nonstoichiometric, containing about 1 at% excess As over those grown at conventional temperature [3] (~600°C) and a high concentration of As-antisite defect [4]. The extremely short photoexcited carrier lifetime (~150 fs) [5] measured in LT GaAs makes it suitable for integrated subpicosecond optoelectronic switching. Upon post-growth annealing at 600°C, the excess As precipitates into clusters [7] and the annealed LT GaAs exhibits very high resistivity which is desirable for many device applications.

Warren et al. [8] proposed a simple model which assumed that the observed As precipitates were metallic and that the Schottky barrier height of As to GaAs held. Therefore, the control of precipitate density and position during annealing period has become an important issue in the point of device applications. Arsenic precipitates are found to form preferentially inside GaAs regions for LT GaAs/AlGaAs heterostructure [9] and inside InGaAs regions for LT GaAs/InGaAs heterostructure [10]. The accumulation and depletion of As precipitates can also be achieved by

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incorporation of impurity [11,12]. Up to now, the study of As precipitate distribution is performed by transmission electron microscope (TEM). In this work, the high-resolution double-crystal X-ray diffraction is used to characterize the redistribution of As precipitates in the Si δ-doped LT GaAs. The superlattice satellite peaks in the rocking curve are observed for annealed samples. The evolution of satellite peak intensity can reveal the degree of As precipitates confined on the Si δ-doped planes, as confirmed by the TEM observations. The asymmetry of X-ray rocking curve intensity indicates the modulation in the lattice parameter of the annealed LT materials after annealing.

2. Experiment

The films used in this work were grown in a Varian GEN II MBE system using element solid source and tetramer As_4. The growth rate was 1.0 μm/h for GaAs with an As_4/Ga flux ratio (beam equivalent pressure) of 24. The substrate was nominally undoped semi-insulating (100) GaAs. Following native oxide desorption at 580°C, a 0.3 μm GaAs buffer layer was deposited at 600°C to smooth the surface. The growth was then interrupted while maintaining the As_4 flux and the substrate temperature was ramped down to 230°C at which the Si δ-doped LT-GaAs structure was grown. The low temperature structure consists of six Si δ-doped layers which are separated by 80 nm GaAs. The Si sheet density is 1.2×10^{13} cm^{-2}. An identical structure but grown at 600°C is used as the control sample. After growth, the samples were cleaved into pieces and annealed for 10 min at the temperature range of 600–900°C in a forming gas ambient and with a GaAs proximity cap. The high-resolution X-ray diffraction measurements were carried out with a Philips DCD-3 double-crystal diffractometer, equipped with a GaAs (004) as the first crystal. A JEM 2000FX electron microscope was used to examine the distribution of As precipitates. Cross-sectional samples parallel to {110} planes were prepared by mechanically thinning and Ar ion milling at low temperature for TEM observations.

3. Results and discussion

3.1. X-ray characterization

Figs. 1a–1e show the (004) X-ray rocking curves for the Si δ-doped LT GaAs structure in the as-grown state and after annealing at 600, 700, 800, and 900°C for 10 min, respectively. For the as-grown sample (Fig. 1a), the perpendicular lattice mismatch in the LT GaAs layer is about 0.12% larger than the bulk GaAs substrate. The expansion of lattice constant of the as-grown LT GaAs is caused by the large concentration of As-antisite defects [4,13] incorporated during the film growth. The presence of well-defined interference fringes in the X-ray rocking curve confirms the high quality of the LT-epitaxial layers because the Pendellösung fringes occur only for high quality thin layers. After annealing at 600°C, the lattice constant reduces and is very close to that of bulk GaAs, as shown in Fig. 1b. The contraction of lattice constant after post-growth

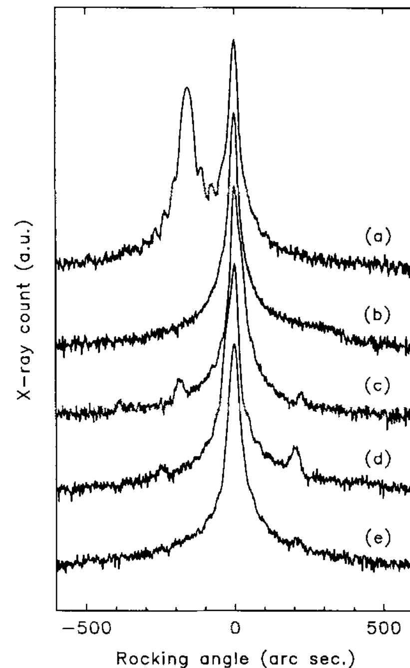

Fig. 1. (004) double-crystal X-ray rocking curves for Si δ-doped LT GaAs under various annealing temperatures: (a) as-grown, and (b) 600, (c) 700, (d) 800, (e) 900°C annealed for 10 min.

annealing can be explained by the removing of the As-antisite defects and formation of Ga vacancies in the epitaxial layer during annealing period [13]. A striking feature in the rocking curves of both 700 and 800°C annealed samples is the presence of satellite peaks with asymmetric intensity around the main (004) GaAs peak, as shown respectively in Figs. 1c) and 1d). The satellite peaks intensity become very weak for sample annealed at a higher temperature of 900°C (Fig. 1e). To clarify that the satellite peaks are not due to the Si δ-doped planes, X-ray analysis was also performed on the controlled wafer. The rocking curve shows only one peak due to Bragg reflection from GaAs layer. The superlattice period Λ was averaged over the positions of the satellite peaks to be about 86 nm according to the equation [14]

$$(2 \sin \theta_n - 2 \sin \theta_{SL})/\lambda(\mathrm{Cu\ K}\alpha_1) = \pm n/\Lambda.$$

The calculated period is close to the nominal undoped LT GaAs spacing of 80 nm between the Si δ-doped layers.

The dependence of the first-order satellite peak intensity on the annealing temperatures is shown in Fig. 2. The intensities first show an increase with annealing temperatures and gradually reach the maximum value at 800°C. However, when annealed at higher temperatures, the intensities begin to decrease and finally become very weak.

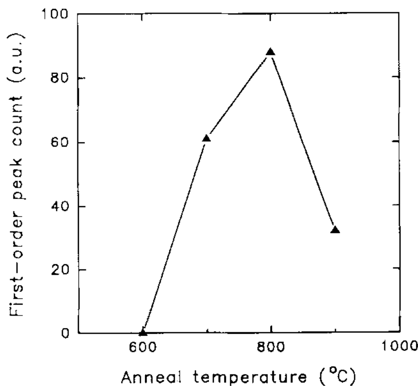

Fig. 2. Dependence of the first order satellite peak intensity on the annealing temperatures for Si δ-doped LT GaAs.

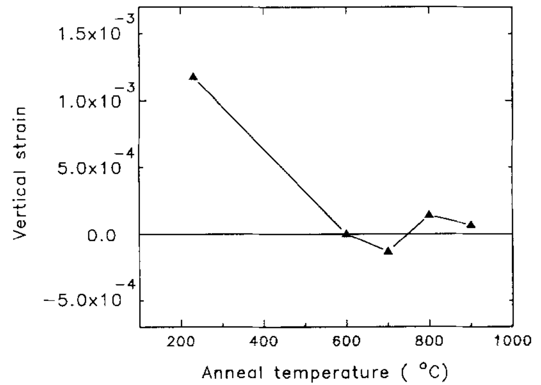

Fig. 3. Average lattice mismatch of the LT epitaxial layer with respect to the GaAs substrate.

In addition to the peak intensity variation as described above, slight shifts of satellite peak positions are observed for samples annealed at different temperatures, indicating the small variation of the average lattice strain in the LT epilayer with respect to the GaAs substrate. Fig. 3 summarizes the average lattice mismatch of the LT structures with respect to the GaAs substrate for different annealing temperatures. The lattice mismatch is calculated from the angular difference between the GaAs substrate peak and the zeroth-order superlattice peak which is derived from the observed first order peaks. It shows a lattice contraction for 700°C annealing and a lattice expansion up to the order of 10^{-4} when annealed at 800 and 900°C. The lattice constant modulation of the epitaxial layers under different annealing temperatures can also be observed from the asymmetrical intensity of the superlattice peaks and GaAs substrate peak as observed in Fig. 1.

3.2. TEM characterization

The evolution of X-ray rocking curves with annealing temperatures, as described above, can be explained consistently by the formation of GaAs/As superlattice due to the accumulation of As precipitates toward the Si δ-doped planes during the annealing period. The accumulation of precipitates may be due to the lower interfacial energy between As precipitate/Si doped GaAs,

compared to that between As precipitate/undoped GaAs. Figs. 4a–4d are the bright-field TEM images of Si δ-doped LT GaAs annealed at 600, 700, 800, and 900°C, respectively. For the 600°C annealed sample, As precipitates of 4 nm in diameter distribute nearly uniformly in the undoped LT-grown GaAs regions with a density of about 1.67×10^{17} cm^{-3}. Also seen is the slight accumulation of precipitates on the Si δ-doped planes. For the 700°C annealed sample, the precipitate coarsens to an average diameter of 16.7 nm on the doped planes. The precipitate density on the δ-doped planes increases with a reduction of the density inside the undoped regions. The periodic structure consisting of alternate GaAs and As precipitates permits a modulation of scattering power [15] along the growth direction and consequently exhibits satellite peaks in the X-ray rocking curve. When annealing temperature increases to 800°C, the As precipitates are totally confined on the Si δ-doped planes, which leaves the undoped regions free of precipitates. The well-defined precipitate/no precipitate region forms the superlattice-like structure and thus leads to the most pronounced satellite peaks in the rocking curve, as shown in Fig. 1d and Fig. 2. When annealed at higher temperature of 900°C, the precipitates further coarsen to about 23 nm. The spacing between the precipitates on the same δ-doped plane is estimated to be 67.5 nm. The large spacing between precipitates reduces the periodicity along the growth direction to the ex-

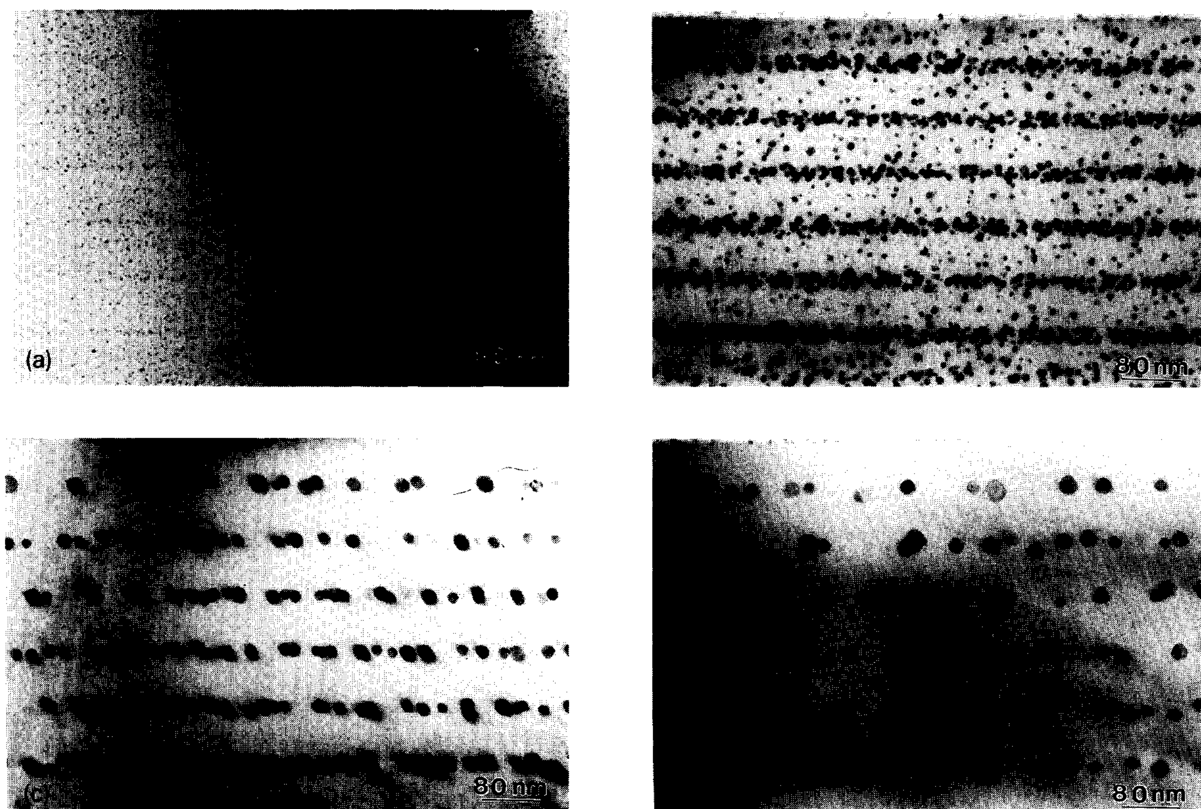

Fig. 4. Bright-field TEM images of Si δ-doped LT GaAs annealed at (a) 600, (b) 700, (c) 800, and (d) 900°C for 10 min.

tent that superlattice peaks are hardly observed in the X-ray rocking curve (Fig. 1e).

4. Conclusion

In this work, we demonstrate the high-resolution X-ray analysis and TEM analysis of Si δ-doped GaAs grown by molecular beam epitaxy at low substrate temperature. The satellite peaks in the X-ray rocking curves are observed for a sample annealed at 700–800°C for 10 min, which is attributed to the formation of GaAs/As superlattice during annealing period. The intensity variation of the satellite peaks reveals the confinement of As precipitates on the Si δ-doped planes, as confirmed by the TEM observation. In contrast to TEM analysis, our results show that high-resolution X-ray analysis can provide a nondestructive and easy way to characterize the diffusion of As precipitates in Si δ-doped LT GaAs. The GaAs/As superlattice will lead to a wide variety of device applications.

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