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Letter to the Editors

Formation of two-dimensional arsenic precipitation in superlattice structures of alternately undoped and heavily Be doped GaAs with varying periods grown by low-temperature molecular beam epitaxy

Z.A. Su[a,*], J.H. Huang[b], W.-I. Lee[a]

[a] *Department of Electrophysics, National Chiao Tung University, Hsinchu, Taiwan, ROC*

[b] *Materials Science Center, National Tsing Hua University, Hsinchu, Taiwan, ROC*

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Abstract

As precipitates in superlattice structures of alternately undoped and $[\mathrm{Be}] = 2.4 \times 10^{20}\ \mathrm{cm}^{-3}$ doped GaAs with varying periods grown by molecular beam epitaxy at low substrate temperatures were studied by transmission electron microscopy. Novel arsenic precipitate microstructures were observed in annealed samples, including preferential accumulation of precipitates inside the Be-doped GaAs but near each interface of Be-doped GaAs and the following grown undoped GaAs. The confinement reaches the extreme for samples annealed at 800°C, where the precipitates appear as dot arrays along such interfaces and leave other areas almost free of precipitates. The incorporation of substitutional Be acceptors is believed to cause a smaller lattice constant in the heavily Be-doped regions than in the undoped regions. A strain-induced mechanism was proposed to account for the preferential segregation of As clusters, though the underlying mechanism is not fully clear. © 1998 Elsevier Science B.V. All rights reserved.

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GaAs and AlGaAs grown by molecular beam epitaxy (MBE) under normal conditions but at low temperatures (LT) have been reported to have unique electronic [1] and optical [2] properties. The LT materials are very nonstoichiometric, containing about 1 at% excess As over those grown at conventional temperature [3] ($\sim$600°C) and are highly strained due to the excess As in the form of antisites and interstitials resulting in a dilated

* Corresponding author. Tel.: + 886 3 5715131; fax: + 886 3 3633429; e-mail: u8221807@cc.nctu.edu.tw.

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lattice detectable with X-ray diffraction [4,5]. Upon post-growth annealing, the excess As segregates, nucleating homogeneously to form a mixture of GaAs matrix and As precipitates [6] accompanied by the relaxation of strain. The degree of nonstoichiometry, and hence the resulting precipitate volume, decreases with increasing growth temperature [7].

The annealed LT GaAs and AlGaAs are semi-insulating [7], a property that has been exploited for various device applications [8–11]. The insulating property can be explained as the result of overlapping depletion regions generated by the Schottky barrier at each precipitate/GaAs interface [12]. Therefore, the ability to tailor the As precipitate sizes and densities through the precipitate coarsening process is quite useful in controlling the electrical and optical properties of LT materials. In addition, it would be useful to be able to control the positioning of the precipitates in the LT epilayers. For AlGaAs/GaAs and InGaAs/GaAs heterostructures grown at low substrate temperatures and subsequently annealed, it has been observed that the As precipitates form preferentially in the GaAs regions [13] and InGaAs regions [14], respectively. Another technique for controlling the positioning of the As precipitates is through the controlled incorporation of impurities. It was found that the As precipitates form preferentially on planes of Si and In while forming preferentially between planes of Be and Al [15,16]. In this letter, we report the first observation of dot arrays of As precipitates in heavily Be-doped GaAs/undoped GaAs superlattice structures with varying periods grown at low substrate temperatures by MBE. In this work, the distribution of As precipitates is found to form two-dimensional arrays only at interfaces of Be-doped GaAs and the following undoped GaAs and leave other areas free of As precipitates.

The samples used in this work were grown on nominally undoped semi-insulating (0 0 1)GaAs by a Varian GEN II MBE system, with an As_4/Ga beam equivalent pressure ratio of 15 as measured with an ion gauge in the substrate growth position. Growth rates for GaAs and AlAs were 0.7 and 0.3 μm/h, respectively. Two Ga effusion furnaces were used (with each contributing one-half of the

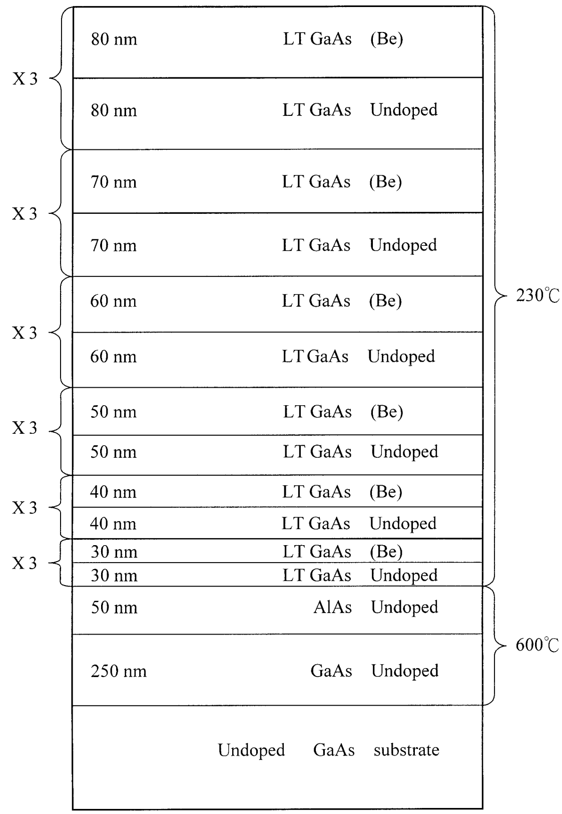

Fig. 1. Schematic superlattice structures of alternately undoped and heavily Be-doped GaAs.

flux). Following the desorption of native oxide at 580°C, a 0.25 μm GaAs buffer layer was first grown at 600°C and then a 50 nm AlAs layer was grown at the same temperature as a marker for later transmission electron microscope (TEM) observations. Growth was then interrupted and the substrate temperature was lowered to 230°C. The structures, as shown in Fig. 1 consisted of six parts. Each part contains a three-period 'superlattice' of layers alternately nominally undoped and doped with Be to an intended concentration of 2.4×10^{20} cm^{-3}. The individual layers in the six parts were 30, 40, 50, 60, 70 and 80 nm thick, respectively. After the growth, the sample was cleaved into pieces, which were annealed with a proximity cap at 600, 700 and 800°C for 30 s under N_2 ambient using an automated rapid thermal annealing (RTA) oven by AG Associates.

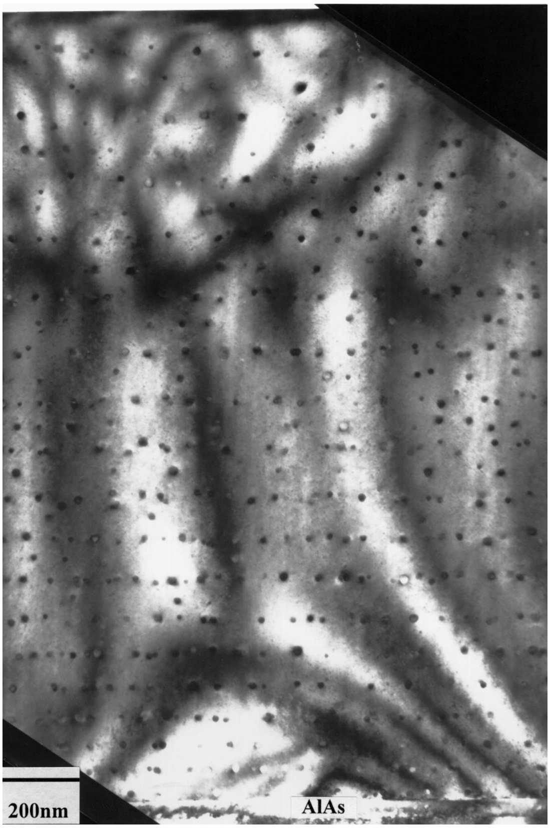

Fig. 2. [1 1 0] cross-sectional bright field TEM image of sample after annealing for 30 s at 800°C.

To investigate the effects of heavily Be doping on the lattice constant, a control sample consisting of a 0.5 μm undoped GaAs layer followed by a 0.5 μm layer of heavily Be-doped GaAs ($2.4 \times 10^{20}\ cm^{-3}$) was also grown under the same growth condition.

Precipitate microstructures in annealed samples were studied by transmission electron microscopy (TEM). [0 1 1] cross-sectional samples were prepared by Ar-ion thinning technique and examined by using a Jeol JEM-2010 transmission electron microscope. Fig. 2 shows the TEM image of sample annealed at 800°C where the precipitates appear as dark spots. In this image, the As precipitates seem to form 'dot arrays' spontaneously and have nearly spherical shapes with diameters in 15–20 nm. This leaves areas between the precipitate accumulation lines almost free of precipitates except a line of precipitates nucleating at the AlAs/undoped GaAs layer interface. The distances between two consecutive precipitate arrays in each part are close to the nominal superlattice period. The bright zone seen at the bottom of the pictures is the AlAs layer, which thus provides a good marker for the start of the periodic structure. These precipitate arrays have been identified to locate inside the Be-doped GaAs but near each interface of the Be doped GaAs and the following grown undoped GaAs, namely, the interfaces of the superlattice periods. In comparison with TEM image of sample annealed at 800°C, the accumulation of As precipitates appears less distinct for the sample annealed at 600°C (not shown) because of the insufficient formation energy. There is no appreciable difference in the TEM images between samples annealed at 700 and 800°C.

It has been shown by Melloch et al. [15] that As precipitates preferentially form in Si-doped GaAs then intrinsic and least favorably in Be-doped GaAs for moderately doped GaAs ([Si], [Be] $< 5 \times 10^{18}\ cm^{-3}$). The present results of As precipitates accumulation in Be-doped GaAs but near each interface of Be-doped GaAs and the following grown undoped GaAs are then contrary to the observations of Melloch et al. Previous study of heavily Si-doped GaAs ($[Si] = 1 \times 10^{19}\ cm^{-3}$) by O'Hagan et al. [17] also showed a different precipitation process from that observed by Melloch et al. It was shown that As precipitates accumulation occurred in the area of undoped regions instead of in the area of heavily Si-doped regions. Consequently, these observations suggest a different trend of As precipitation process in heavily doped GaAs (either doped with Si or Be) than in the moderately doped GaAs.

Several mechanisms [13,18,20,21] have been proposed to account for the preferential accumulation of As precipitates in some regions. For this study, we propose that the preferential segregation of As clusters is a strain-induced process and the reasoning is explained below. Room-temperature measurements of Raman spectra on heavily Be-doped (in $10^{19}\ cm^{-3}$ range) GaAs by Bliss et al. [19] have shown that a significant fraction of the total Be, greater than 50%, must occupy substitutional

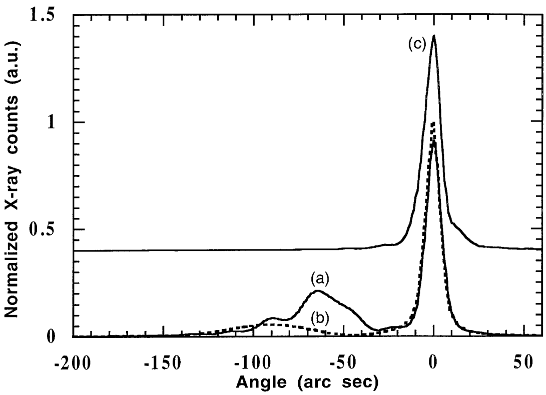

Fig. 3. (0 0 4) double-crystal X-ray rocking curves for as-grown control sample (a) before, (b) after etching off the top Be-doped GaAs layer showing the effect of high Be doping on the lattice constant of LT GaAs, and (c) after annealing at 800°C for 30 s before etching.

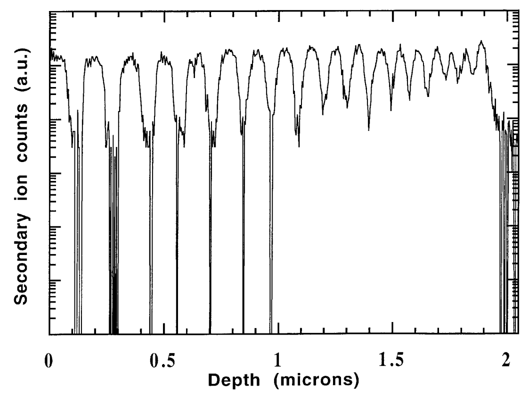

Fig. 4. Secondary ion mass spectra of Be after the annealing at 800°C for 30 s.

positions. The amount of excess As incorporation in LT GaAs is thereby suppressed due to the exclusive occupation of Be on Ga sites. As a result, the degree of lattice dilation due to the As_{Ga} (and probably As interstitials) defects in as-grown LT GaAs would be reduced. The X-ray rocking curve of the control sample actually shows the effect of Be doping on lattice parameter. As shown in Fig. 3a two diffraction peaks other than the substrate peak (one with the strongest intensity) can be clearly resolved. By comparing with the diffraction peaks (Fig. 3b) of undoped GaAs layer by etching off the top Be-doped GaAs layer, the weaker peak has been identified to be due to the Bragg reflection of the undoped GaAs layer, and thereby the other peak corresponds to the Be-doped GaAs layer. After annealing at 800°C for 30 s, only the substrate peak can be observed (Fig. 3c). This indicates that the undoped LT GaAs has a larger lattice constant than the heavily Be-doped LT GaAs. There is no appreciable difference in secondary ion mass spectra (SIMS) profiles of Be between samples before (not shown) and after annealing at 800°C (shown in Fig. 4). It indicates that the Be diffusion in heavily doped GaAs [22] in this case need not be taken into account. Owing to the difference in lattice constants, the strain or mismatch with respect to the substrate at interfaces of Be-doped GaAs and the following grown undoped GaAs is stronger than that at other interfaces. Upon annealing, excess As then diffuse to the interfaces where the larger strain exists to relieve the strain, resulting in the strong accumulation of As precipitates in these regions. Line of precipitates at the interface of high-temperature grown AlAs and the first epilayer may also be responsible for the relaxation of strain energy. Further work is needed to fully understand the mechanism of As precipitation process observed in this study.

In summary, we have grown superlattice structures of alternately undoped and heavily Be-doped GaAs with varying periods by MBE at a substrate temperature of 230°C. Upon subsequently annealing, As precipitates formed preferentially inside the Be-doped GaAs but near each interface of Be-doped GaAs and the following grown undoped GaAs. The confinement reaches the extreme for sample annealed at 800°C, where the precipitates appear as dot arrays along the such interfaces. We believe this is caused by the larger strain at these interfaces due to the smaller lattice constant in the heavily Be-doped GaAs than in the undoped GaAs. This ability to control As precipitates into dot arrays in LT materials may lead to useful device applications.

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