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Strain-enhanced arsenic precipitation in GaAs-based quantum-well structures grown by low-temperature molecular beam epitaxy

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Abstract
The precipitation of arsenic in InGaAs/GaAs and GaAs/AlGaAs multiple-quantum-well (MQW) structures grown by molecular-beam epitaxy at 230 °C has been studied by transmission electron microscopy. For InGaAs/GaAs MQWs with strained InGaAs wells, upon annealing at 500 and 600 °C, arsenic precipitates tend to be completely confined in InGaAs wells near the InGaAs/GaAs interfaces, resulting in dual two-dimensional planes of precipitates in each InGaAs well. In contrast, this strong confinement of precipitates does not exist in InGaAs/GaAs MQWs with partially or totally strain-relieved InGaAs wells and in unstrained AlGaAs/GaAs MQWs. The present results suggest that the As precipitation process in strained GaAs-based MQWs is not only driven by the bond strength in different materials, but also by the lattice-mismatch-induced strain.

1. Introduction

Low-temperature molecular-beam epitaxy (LT-MBE) is a thin-film deposition technique that allows one to work far from equilibrium. This approach has recently been adopted to prepare GaAs-based diluted magnetic semiconductors (DMSs) [1], e.g., (Ga, Mn)As, while it was first used to prepare a truly insulating GaAs buffer epilayer to eliminate the side-gating effects in GaAs field-effect transistor circuits [2]. The LT-GaAs contains about 1 at.% excess arsenic [2] compared with those grown at conventional temperatures (∼600 °C), and a high concentration of defects accommodated principally as As antisites (As_{Ga}) and Ga vacancies (V_{Ga}) [3]. Upon

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post-growth annealing above ∼500 °C, the excess arsenic forms precipitates embedded in the LT-GaAs matrix, and the LT-GaAs becomes highly resistive [4].

As-grown LT-GaAs is crystalline but it has a lattice enlarged by ∼0.1% with respect to GaAs [4]; however, annealed LT-GaAs is nearly lattice-matched to GaAs [5]. As a result, the precipitation of excess As in annealed LT-GaAs can be ascribed to a strain-relief-related process. Several studies have shown that the redistribution of As precipitates in LT materials during annealing can be tailored to certain extents by using techniques such as selective doping and heterostructures [6–8]. In this regard, it was found that As precipitates form preferentially inside the well regions for LT-GaAs-based multiple-quantum-well (MQW) structures [6, 7], or preferentially form in Si-doped LT-GaAs, then intrinsic GaAs, and least favourably in Be-doped LT-GaAs [8]. A general V_{Ga}-assisted As_{Ga} diffusion mechanism has been proposed to model the redistribution of As precipitates in annealed LT materials [9–13]; that is, As_{Ga} tends to diffuse to vacancy-rich regions to form precipitates. Recently, as another aspect, we demonstrated that the strain caused by the lattice mismatch between LT epilayers might enhance the As precipitation in certain regions [14]. In this paper, we present further evidence of the effect of lattice-mismatch-induced strain on As precipitation in LT-GaAs-based MQW structures. We found that, upon annealing at 500 and 600 °C, As precipitates not only preferentially accumulated in the InGaAs wells, a phenomenon already reported previously [7], but were further completely confined near the InGaAs/GaAs interfaces in strained LT-InGaAs/GaAs MQWs. Consequently, dual two-dimensional planes of As precipitates were formed in each InGaAs well near the strained InGaAs/GaAs interfaces. In contrast, in totally or partially strain-relaxed LT-InGaAs/GaAs MQWs and in unstrained LT-GaAs/AlGaAs MQWs, this phenomenon of complete confinement of As precipitates along the well/barrier interfaces did not exist. The present results clearly demonstrate a strain-enhanced As precipitation process.

2. Experimental details

In this work, three LT-GaAs-based MQW structures were grown in a Varian Modular GEN II MBE system on semi-insulating GaAs(001) substrates with an As_4/Ga beam equivalent pressure ratio of 25. All samples began with the growth of a GaAs buffer layer and an $Al_{0.26}Ga_{0.74}As$ or AlAs marker layer at 600 °C, followed by the growth of LT-GaAs-based MQWs at 230 °C. The substrate temperature at which the LT structure was grown was measured by a thermocouple located at the centre of the substrate heater. Since the pyrometer used for this study was specialized for monitoring the GaAs or InP temperature within the range 400–1000 °C in an MBE environment, the thermocouple had been calibrated by the pyrometer at a high-temperature range (>450 °C) for each of the sample growths. Based on the plot of the pyrometer reading (T_{py}) versus the thermocouple reading (T_{th}), the substrate temperature below 400 °C could be estimated by extrapolating the T_{py}–T_{th} curve into the low-temperature range. The layer structures of LT-GaAs-based MQWs are schematically shown in figures 1(a)–(c). Sample A consists of six 30 nm thick $In_{0.13}Ga_{0.87}As$ wells separated by 30 nm thick GaAs barriers. Sample B contains a 30 nm GaAs cap layer and three 3-period GaAs/$Al_{0.23}Ga_{0.77}As$ MQWs, with nominal well and barrier thickness of 30, 40, and 50 nm, respectively. Sample C, from the top, contains a 30 nm GaAs cap layer and four $In_{0.13}Ga_{0.87}As$ wells with varying widths of 60, 50, 40, and 30 nm, respectively, separated by 60 nm thick GaAs barriers. After growth, all samples were cleaved into pieces and annealed at 500–800 °C for 30 s, in N_2 ambient and with a proximity cap, by rapid thermal annealing. The redistribution of As precipitates in annealed samples was examined by transmission electron microscopy (TEM). Cross-sectional samples parallel to [110] planes were prepared conventionally by mechanical thinning and Ar-ion milling.

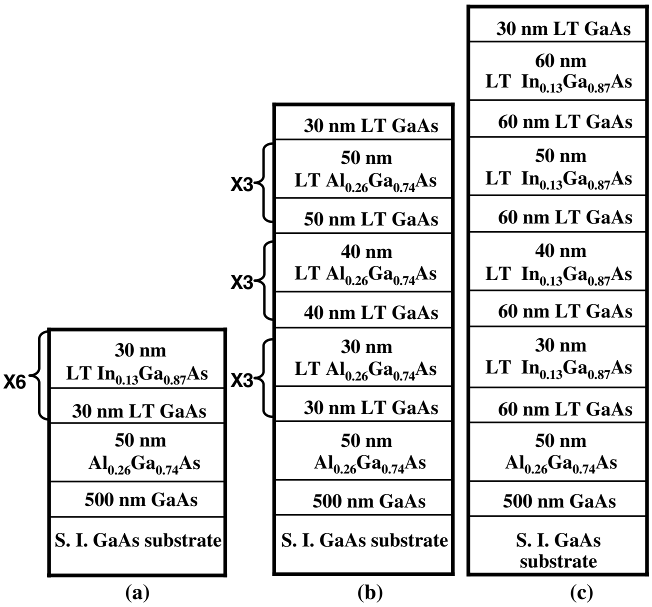

Figure 1. Schematic structures of three LT-GaAs-based MQWs: (a) 6-period strained $In_{0.13}Ga_{0.87}As$/GaAs MQWs with nominal well and barrier of 30 nm thickness, (b) three 3-period unstrained GaAs/$Al_{0.23}Ga_{0.77}As$ MQWs with nominal well and barrier of 50, 40, and 30 nm thickness, respectively, and (c) four $In_{0.13}Ga_{0.87}As$ wells with varying widths of 60, 50, 40, and 30 nm, separated by 60 nm thick GaAs.

3. Results and discussion

Figures 2(a) and (b) show the TEM images of ∼five LT-InGaAs/GaAs MQWs of sample A annealed at 500 and 600 °C, respectively. In these images, the InGaAs wells appear as darker zones compared to the GaAs barriers, and the misfit dislocations possibly caused by the mismatch between InGaAs and GaAs were not found, thereby yielding a strained LT-InGaAs/GaAs MQW structure. In addition, As precipitates, which appear as nearly spherical dark particles, exist only in the InGaAs wells, and further form two rows near the top and bottom interfaces. However, due to the longer diffusion length of excess As at 600 °C than at 500 °C, the precipitates in each array are bigger but less dense for the 600 °C-annealed sample. This is the first demonstration that As precipitates are not only confined in the InGaAs wells but further form dual two-dimensional arrays near the strained InGaAs/GaAs interfaces upon annealing at 500 and 600 °C. This result seems to indicate a different precipitation process from that observed by Cheng *et al* [7]. Although using similar $In_{0.13}Ga_{0.87}As$/GaAs MQW structures as in this work, in Cheng's study the thickness of InGaAs wells varied from 5 to 20 nm, but only single two-dimensional precipitate arrays in each InGaAs well could be observed. We attribute the discrepancy between the two results to the much thinner wells used in Cheng's study. This is because as the precipitates have a size comparable to the well thickness, the locations of confinements cannot be clearly identified. The TEM images (not shown) of sample A annealed at 700 and 800 °C indeed show a precipitate distribution similar to Cheng's work, namely that As precipitates locate more or less near the centre of each well.

Figure 3(a) shows the TEM images of ∼eight GaAs/AlGaAs MQWs of sample B annealed at 500 °C. In the image, As precipitates can be found almost everywhere except in a narrow

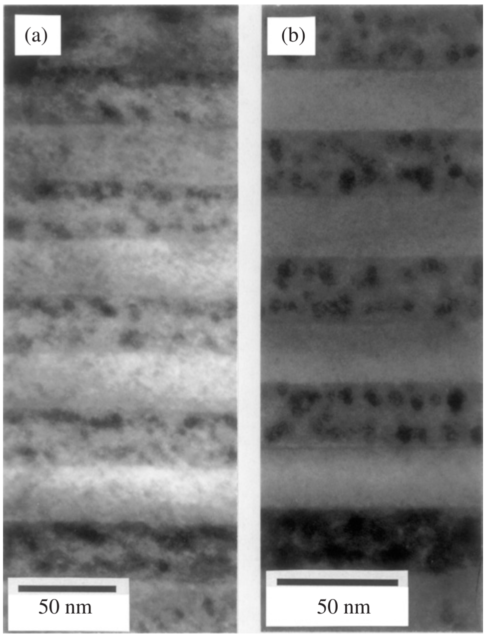

Figure 2. TEM images of the strained LT-$In_{0.13}Ga_{0.87}As$/GaAs MQWs (sample A) annealed at (a) 500 °C and (b) 600 °C for 30 s.

precipitate depletion zone on the AlGaAs side along each AlGaAs/GaAs interface. Also, as the case of sample A, there exist two precipitate arrays of bigger size in each GaAs well near the interfaces. The densities of As precipitates in the interiors of GaAs wells and AlGaAs barriers are approximately the same, indicating that no significant difference of the As concentration exists between the two LT materials. Figure 3(b) is the TEM image of sample B annealed at 600 °C. Compared to figure 3(a), more As precipitates are now confined near the GaAs/AlGaAs interfaces, leaving fewer As precipitates existing in the interiors of the GaAs wells and AlGaAs barriers. The further annealing at 700 °C, nevertheless, causes the As precipitates to be totally confined in the GaAs wells. The As precipitation in annealed sample B as observed in figure 3 is similar to that previously presented by Mahalingam *et al* [6], although a smaller dimension of quantum-well structure is used in this study.

The As precipitation as observed in figures 2 and 3 shows a tendency to occur in the well regions of both strained and unstrained GaAs-based MQWs. The driving force of As diffusion across a heterointerface has been suggested to be a difference in the precipitate/matrix interfacial energy [6] or in the bond strength between the heteroepilayers [12]. The latter mechanism appears to be more intuitive from the free-energy point of view; i.e., the condensation of excess As into precipitates occurs more favourably in materials of lower bond strength. The melting point (and therefore the bond strength) is the weakest for InGaAs and highest for AlGaAs. Upon annealing at a temperature higher than the growth temperature under an As overpressure, the material with lower bond strength tends to contain more column III vacancies, which act as the mediators for the interdiffusion of excess As in the LT materials [12, 13]. Consequently, As precipitates tend to form preferentially in InGaAs wells for InGaAs/GaAs MQWs and in GaAs wells for GaAs/AlGaAs MQWs.

Although a reasonable explanation has been proposed to account for the preferential precipitation in the wells of heterostructures, the direct comparison of precipitation strength

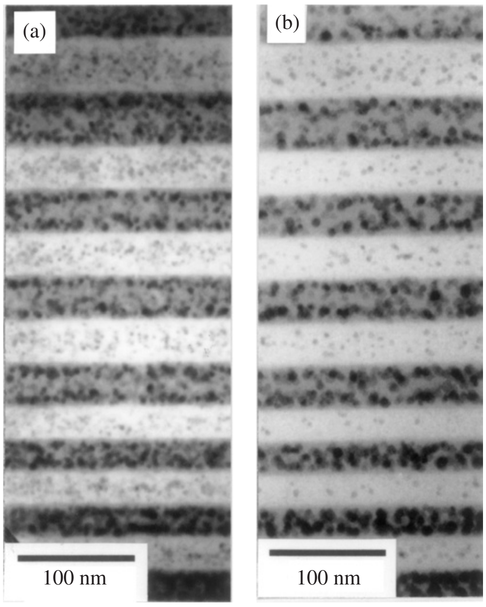

Figure 3. TEM images of the unstrained LT-$Al_{0.23}Ga_{0.77}As$/GaAs MQWs (sample B) annealed at (a) 500 °C and (b) 600 °C for 30 s.

among GaAs-based heterointerfaces has not been reported yet. Assuming that the melting point varies linearly with the amount of GaAs, x, in GaAs-based ternary alloys (this is a reasonable assumption if x is large), the bond-strength difference between $In_{0.13}Ga_{0.87}As$ and GaAs should be relatively lower than that between $Al_{0.26}Ga_{0.74}As$ and GaAs. As a result, a larger Ga-vacancy gradient should exist across the AlGaAs/GaAs interfaces, thereby inducing a stronger precipitation for excess As. However, a comparison of the As precipitation in strained InGaAs/GaAs and unstrained GaAs/AlGaAs MQWs as observed in figures 2 and 3 suggests that the strained InGaAs/GaAs heterointerfaces are the better effective nucleation centres for As precipitates. This is supported by the fact that As precipitates were completely confined near the InGaAs/GaAs interfaces but only partially confined near the GaAs/AlGaAs interfaces. Therefore, one would expect additional driving forces for the much stronger confinement of As precipitates near the strained InGaAs/GaAs interfaces. Considering that the relaxed $In_{0.13}Ga_{0.87}As$ has a larger lattice constant than GaAs by $\sim$1.75%, we propose the lattice-mismatch-induced strain is an indispensable factor that helps induce arsenic precipitation. The reason is that the lattice-mismatch-induced strain is confined to the InGaAs layers alone, especially at the InGaAs/GaAs interfaces for coherent growth. Therefore, upon appropriate annealing, the excess As diffuses to the interfaces and forms precipitates to relieve the strain. However, if the width of the InGaAs well is beyond the critical thickness, most strain is relieved during growth by forming dislocations. Considering the mechanism of particles precipitating and coarsening, these dislocations are effective nucleation centres for As precipitates during the anneal. Therefore, one would expect larger precipitates form around dislocations, and thereby the confinement of precipitates no longer exists.

The TEM image of the 700 °C-annealed sample C shown in figure 4 confirms the foregoing arguments further. It can be seen that for the 30 nm thick InGaAs well, there exists only a single As precipitate array located near the centre of the well, as in the case of sample A when annealed at 700 and 800 °C. For the 40 nm thick InGaAs well, two As precipitate arrays located

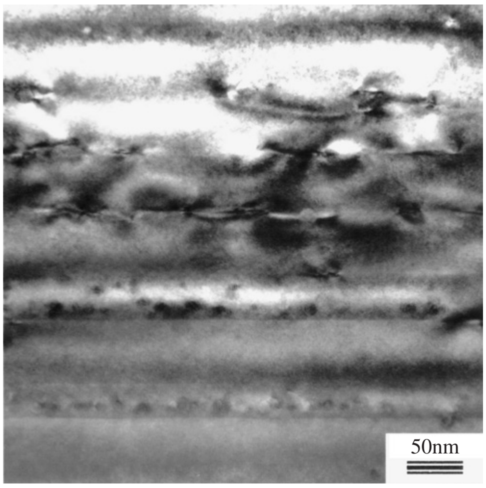

Figure 4. TEM image of sample C annealed at 700 °C for 30 s. The 30 nm thick InGaAs well contains only a single array of precipitates, while the 40 nm thick InGaAs well contains dual precipitate arrays located near each InGaAs/GaAs interface. However, the precipitation in the other two wider InGaAs wells cannot be well observed due to the formation of dislocations.

near the top and bottom InGaAs/GaAs interfaces can be clearly observed, due to the wider width of the well. However, for the other two wider wells (thicker than 40 nm), dislocations accompanied by larger precipitates appear due to the partial or total relaxation of strain, and the confinement of precipitates near interfaces no longer exists. Figure 4 clearly shows the effect of the lattice-mismatch-induced strain on the As precipitation process in InGaAs/GaAs MQWs. In contrast, the preferential precipitation in GaAs/AlGaAs MQWs may be mainly driven by the difference in bond strength between GaAs and AlGaAs, though a very slight strain ($\sim$0.03%) also exists in AlGaAs barriers.

4. Conclusions

In summary, we have studied the redistribution of As precipitates in annealed GaAs/InGaAs and GaAs/AlGaAs MQWs grown by MBE at a substrate temperature of 230 °C. For strained LT-GaAs/InGaAs MQWs, upon annealing at 500 and 600 °C, As precipitates formed completely inside the InGaAs regions and they were further confined in quasi two-dimensional planes near the GaAs/InGaAs interfaces. This phenomenon was not observed in partially or totally strain-relieved LT-GaAs/InGaAs MQWs due to the formation of misfit-induced dislocations. The utter confinement of precipitates near the heterointerfaces does not exist in unstrained AlGaAs/GaAs MQWs; instead, As precipitates are dispersed randomly in both the GaAs and AlGaAs layers. Our results show that the As precipitation process in strained GaAs-based MQWs is not only driven by the bond strength difference between the heteroepilayers but also by the lattice-mismatch-induced strain. The ability to control the As precipitates into two-dimensional planes in LT materials should lead to many useful applications, such as metal-based transistors, long-wavelength optical detectors, and other novel quantum-dot-based devices.

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