Molecular beam epitaxy of high-quality, nonstoichiometric multiple quantum wells

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(Received 18 September 1995; accepted 11 October 1995)

Multiple quantum wells (MQWs) have been grown at low substrate temperatures by molecular beam epitaxy so as to incorporate excess arsenic. This excess arsenic precipitates and preferentially coarsens to the lower band gap well regions with anneal. Despite the excess arsenic, these AlAs/GaAs MQW structures exhibit sharp excitonic features that are comparable to those exhibited by stoichiometric MQW structures grown at standard temperatures. In addition to the sharp excitonic transitions, these MQWs possess ultrafast recombination lifetimes making them attractive for photorefractive, electro-optic sampling, and saturable absorption applications. © *1996 American Vacuum Society.*

I. INTRODUCTION

When arsenides—such as GaAs or AlGaAs—are grown at low substrate temperatures by molecular beam epitaxy (MBE), excess arsenic can be incorporated into the lattice.[1] In spite of excess arsenic volume fractions as high as 1%–2%, the crystal can exhibit high structural quality.[2] With anneal, the excess arsenic precipitates, forming a composite of semimetallic arsenic clusters in an arsenide semiconductor matrix.[3] With further anneal, the arsenic clusters coarsen.[4] One can control the composite by use of the substrate temperature during MBE to set the amount of excess arsenic in the crystal,[5] and the anneal temperature to determine the final spacing of the arsenic clusters.[4,6] The electrical and optical characteristics of these composites have been investigated and exploited for many device applications.[7]

When the average spacing between the arsenic clusters is about 3 Bohr diameters, these composites exhibit enhanced electro-optic properties, much stronger than the quantum-confined Stark effect in high-quality, highly stoichiometric, multiple quantum well (MQW) structures.[8] When low-temperature grown (LTG) MQW structures are annealed, the arsenic precipitates preferentially coarsen to the narrow band gap material.[6,9,10] Since the arsenic clusters are semimetallic, and deplete the surrounding semiconductor, this would result in a semi-insulating MQW that would also have picosecond lifetimes—an attractive material for electro-optic applications. However, previous reports of LTG/MQW structures indicated the excitons were too severely broadened for useful applications.[11] Since one can vary the amount of excess arsenic in the epilayers and the amount of arsenic precipitation and coarsening that occurs, there is a broad spectrum of LTG materials. We have recently achieved sharp optical transitions of quantum-confined excitons in AlAs/GaAs LTG MQWs.[12] In this article we compare AlAs/GaAs multiple quantum wells grown at standard temperatures, low temperatures, and low temperatures where the GaAs wells are grown by MBE and the AlAs barriers by migration-enhanced epitaxy (MEE).[13]

II. COMPOSITE FORMATION

The MQWs all had 10-nm-thick GaAs quantum wells and the AlAs barriers ranged from 2 to 3.5 nm. They were grown in a GEN II MBE system using the tetramer form of arsenic, As_4, and an As_4 to Ga beam-equivalent pressure of about 20. The growth rate for the GaAs wells was 1 μm/h and the growth rate for the AlAs barriers was 0.3 μm/h. The MQW referred to as the standard temperature grown (STG) sample consisted of 150 periods with 3.5 nm AlAs barriers grown at a substrate temperature of 600 °C on an n^+GaAs substrate. The MQW referred to as the low temperature grown sample (LTG) consisted of 150 periods with 3.5 nm AlAs barriers grown at a substrate temperature of 310 °C on an n^+GaAs substrate. Two samples were grown where the GaAs wells were grown by MBE and the AlAs barriers were grown by MEE. These samples will be referred to as LTG/MEE sample 1, which consisted of 80 periods with 2.5 nm AlAs barriers

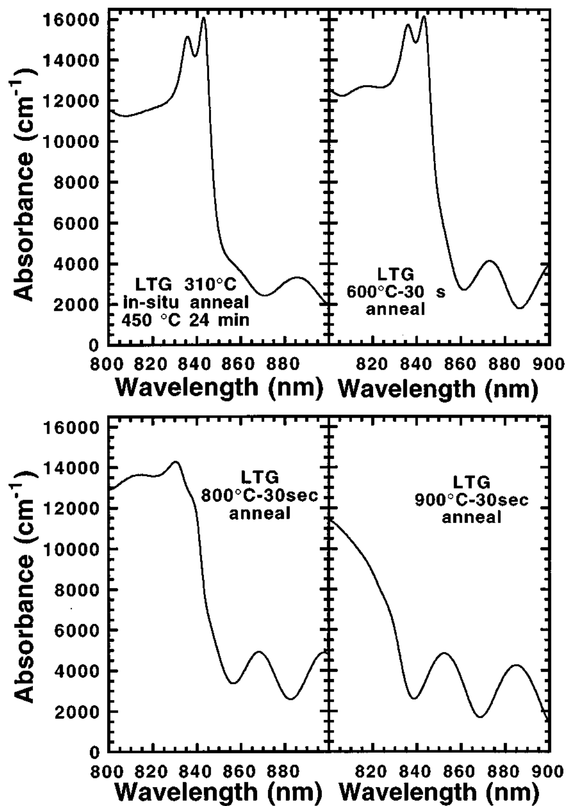

FIG. 1. Absorbance as a function of anneal for the LTG MQW sample. This sample was grown at a substrate temperature of 310 °C. This MQW was incorporated in a *p-i-n* structure. Since the top *p* region was grown at 450 °C and required 24 min, much of the excess arsenic has precipitated. Sharp excitonic features are observed for the *in situ* annealed sample and the 600 °C 30 s annealed sample.

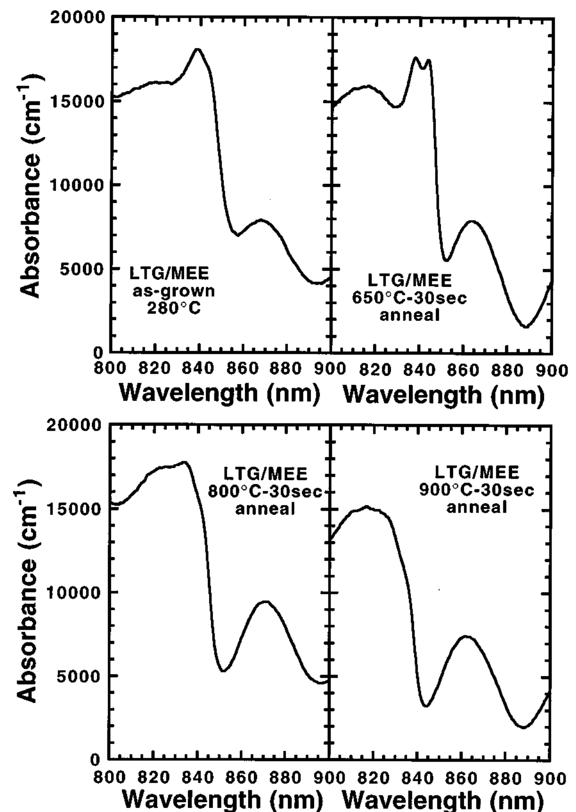

FIG. 2. Absorbance as a function of anneal for the LTG/MEE MQW. This sample was grown at 280 °C with the GaAs wells grown by MBE and the AlAs barriers by MEE. Therefore the AlAs barriers are stoichiometric and the GaAs wells nonstoichiometric. Since this sample did not experience an *in situ* anneal, all the excess arsenic is in the form of point defects. Only after anneal, and precipitation of the excess arsenic, do sharp excitonic absorption features appear.

grown at a substrate temperature of 280 °C on an n^+GaAs substrate, and LTG/MEE sample 2, which consisted of 80 periods with 2 nm AlAs barriers grown at a substrate temperature of 290 °C on a semi-insulating GaAs substrate. The STG and LTG MQWs were incorporated in *p-i-n* structures. The top *p* regions, which consisted of 200 nm of *p*-$Al_{0.3}Ga_{0.7}As$ and 200 nm of *p*-GaAs, were grown at a substrate temperature of 450 °C on the LTG MQW sample, which acted as a precipitation anneal of 24 min for the excess arsenic in the LTG MQW. The LTG/MEE MQW samples did not experience an *in situ* anneal.

After epitaxy, the wafers were cleaved into samples. An AG Associates Mini-Pulse Rapid Thermal Processor was used to anneal samples at temperatures ranging from 600 to 900 °C for 30 s using a GaAs proximity cap. So that absorption measurements could be performed, the substrates were removed from some samples. An $Al_{0.5}Ga_{0.5}As$ layer 0.5 μm thick was used as an etch stop layer so the GaAs substrate could be removed using a wet etch of 10:1 hydrogen peroxide:ammonium hydroxide.

III. CHARACTERIZATION

The near band edge absorption is shown as a function of anneal in Fig. 1 for the LTG sample and in Fig. 2 for LTG/MEE sample 1. These samples did not have antireflection coatings, so Fabry–Perot fringes are present. For the LTG sample, clearly defined light- and heavy-hole excitonic absorptions are seen at room temperature for the 450 °C 24 min annealed sample, and the sample that had the additional 600 °C 30 s anneal. However, for higher temperature anneals (>700 °C) the excitonic features become broadened and reduced in intensity. We have identified this reduction in the excitonic absorption features with anneal as being due to interface intermixing.[14,15]

Since the LTG sample had a 450 °C 24 min *in situ* anneal, significant precipitation of the excess arsenic has occurred. In contrast, after epitaxy the LTG/MEE samples have all the excess arsenic in the form of point defects. Therefore in Fig. 2 for the as-grown LTG/MEE sample, the excitonic absorption becomes more defined after the 650 °C 30 s anneal. We have previously observed the emergence of excitonic absorption in both bulk LTG GaAs and LTG AlGaAs materials as the arsenic point defects disappear with anneal.[8] In spite of the fact that the AlAs barriers are stoichiometric for the as-grown LTG MEE sample, the excitonic absorption broadens and reduces in intensity with further anneal. However, it should be noted that since the LTG MQW was grown at

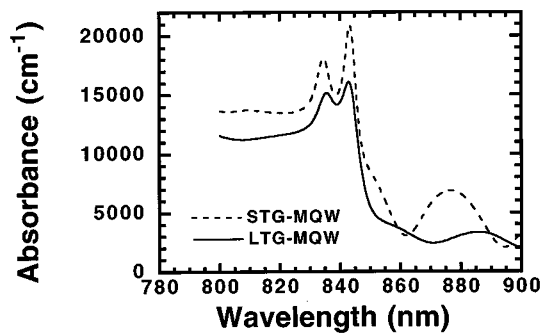

FIG. 3. Comparison of absorbance for a LTG and a STG MQW.

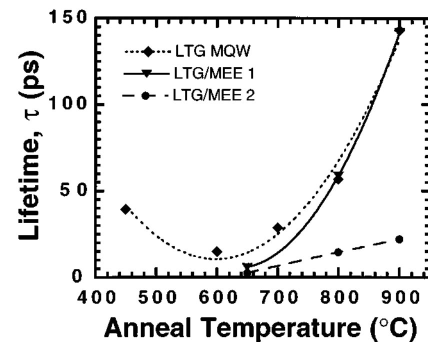

FIG. 5. Carrier lifetime as a function of anneal for the LTG and LTG/MEE MQW samples.

310 °C and the LTG/MEE MQW was grown at 280 °C, there is considerably more excess arsenic in the GaAs regions of the LTG/MEE MQW as compared to the LTG MQW.

In Fig. 3 the band edge absorption is compared for the STG MQW and the LTG MQW 450 °C 24 min annealed sample. Clearly seen is that the excitonic features for the LTG MQW are comparable to those for STG MQW material. The heavy-hole transition in the LTG MQW has a full width at half-maximum (FWHM) of 10 meV while the heavy-hole transition for the STG MQW is only slightly narrower at 6 meV.[14]

The interface perfection and the amount of excess arsenic incorporated in the MQWs were investigated with high-resolution x-ray diffraction using (002) and (004) reflections, respectively. Shown in Fig. 4 is the (002) x-ray data for the STG MQW sample and for LTG/MEE sample 2 as a function of anneal. The LTG/MEE MQW samples 1 and 2 have higher structural quality than the STG MQW as indicated by the narrower linewidths (24 versus 27 arcsec for the $n=1$ peak) and the larger number of x-ray satellite peaks that are observed. With anneal above 650 °C the x-ray peaks reduce in intensity and broaden in linewidth for the LTG/MEE MQW samples due to interface intermixing, as was observed with the excitonic absorption. Interestingly, LTG/MEE MQW sample 2 was found to have more excess arsenic incorporated than LTG/MEE MQW sample 1 and the LTG MQW sample. This was revealed by the larger $n=0$ peak position (-113 versus -90 arcsec) that appeared even though sample 2 has thinner AlAs layers (20 versus 25 Å). This additional arsenic in sample 2 reduces the carrier lifetime.

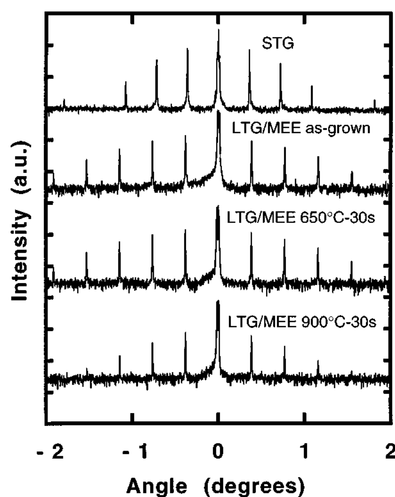

FIG. 4. X-ray diffraction from the STG MQW and LTG/MEE MQW sample 2 as a function of anneal.

The carrier lifetimes in the MQWs were measured using a pump/probe change in absorption technique.[16] The lifetimes as a function of anneal temperature are shown in Fig. 5 for the LTG and LTG/MEE MQW samples. In general the lifetimes increase with anneal. The exceptions seen in Fig. 5 is the reduction in lifetime from 36 ps for the 450 °C 24 min annealed LTG MQW to 15 ps with an additional 600 °C 30 s anneal. The lifetime increases with anneal because point defects are being removed and the arsenic clusters—which are efficient recombination sites—are becoming less dense as they coarsen. For the as-grown LTG/MEE MQW samples considerable trapping occurs at point defects. So although the free carriers disappear on the order of a picosecond, the photogenerated carriers can remain in traps for hundreds of picoseconds, which Fauchet *et al.*[17] have pointed out limits the usefulness of as-grown LTG materials for high-speed photoconductor applications. The LTG/MEE MQW sample 1 that was annealed at 650 °C for 30 s had a lifetime of 6 ps while still displaying sharp excitonic transitions. This combination of sharp excitonic transitions and ultrafast recombination lifetimes is unique to these LTG and LTG/MEE MQWs.

One other point to address concerning Fig. 5 is that the lifetimes of sample LTG/MEE sample 2 increase at a much slower rate with anneal than the LTG MQW sample or LTG/MEE MQW sample 1. In addition, the bandedge absorption of LTG/MEE sample 2 did not exhibit clear excitonic transitions for any anneal condition. LTG/MEE sample 2 was grown on a semi-insulating GaAs substrate at a substrate thermocouple reading of 290 °C, while the LTG MQW sample and LTG/MEE sample 1 were grown on n^+GaAs substrates at substrate thermocouple readings of 310 and 280 °C, respectively. It is possible that some impurity is dif-

fusing out from the semi-insulating substrate and interfering with the epitaxy at these low substrate temperatures. However, from the x-ray data LTG/MEE MQW sample 2 exhibited structural quality superior to that of the STG MQW. It is possible that much more excess arsenic was incorporated into LTG/MEE MQW sample 2. The reason for such additional arsenic could be an actual lower substrate temperature during epitaxy, in spite of comparable thermocouple readings, because of the difference in free carrier absorption of the substrates.

IV. SUMMARY

We have demonstrated high-quality nonstoichiometric MQWs. These MQWs, with the unique combination of sharp excitonic transitions and ultrafast recombination lifetimes, have exciting possibilities for photorefractive, electro-optic sampling, and saturable absorption applications.

ACKNOWLEDGMENTS

This work was supported in part by the MRSEC Program of the NSF under Award No. DMR-9400415. One of the authors (M. R. M.) acknowledges support from the U.S. Air Force Office of Scientific Research under Grant No. F49620-93-1-0031. Another author (D. D. N.) also acknowledges support by the NSF PYI program.

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