Arsenic cluster engineering for excitonic electro-optics

M. R. Melloch
School of Electrical Engineering, Purdue University, West Lafayette, Indiana 47907

D. D. Nolte
Department of Physics, Purdue University, West Lafayette, Indiana 47907

N. Otsuka and C. L. Chang
School of Materials Engineering, Purdue University, West Lafayette, Indiana 47907

J. M. Woodall
IBM Research Division, Yorktown Heights, New York 10598

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An unexpectedly large room-temperature electro-optic effect has been observed in $Al_{0.25}Ga_{0.75}As$ containing As clusters. The room-temperature band-edge absorption of this metal–semiconductor composite exhibits a clearly defined excitonic edge. This band-edge absorption can be strongly affected by electric fields due to exciton life-time broadening; almost a 60% differential transmission was obtained for a 1 μm thick $Al_{0.25}Ga_{0.75}As$ epilayer containing As clusters. This is comparable to values obtained using GaAs/AlGaAs multiple quantum well structures. The excitonic absorption is a strong function of the average As cluster spacing that is controlled with the cluster coarsening anneal temperature. This enhancement of the excitonic optical properties by embedded metallic clusters represents a fundamental departure from traditional quantum well engineering.

I. INTRODUCTION

GaAs and AlGaAs epilayers that are grown by molecular beam epitaxy (MBE) under normal conditions except at very low substrate temperatures (250 °C) can contain an As excess as high as 1.5%.[1] The amount of excess As incorporated into the epilayer is exponentially dependent on the substrate temperature during MBE.[2] Annealing these epilayers at temperatures of 600–900 °C results in the excess arsenic forming clusters in a high-quality GaAs or AlGaAs matrix, which we designate as GaAs:As or AlGaAs:As.[3] The total energy of these two-phase systems is reduced by an increase in size and hence decrease in density of the clusters due to a reduction in total precipitate-to-matrix interfacial area. Therefore the final cluster sizes and densities depend upon how much coarsening occurs during the anneal, which is a function of the temperature and duration of the anneal.[4]

GaAs epilayers containing excess As have already found many useful device applications. As a buffer layer beneath GaAs field effect transistors, GaAs:As eliminates sidegating effects.[5–7] Improved gate-to-drain transistor breakdown has been demonstrated by placing a GaAs epilayer with excess As on top of the channel.[8] Because the As clusters act as internal Schottky barriers and hence are very efficient recombination centers, GaAs:As is a very fast photoconductor. GaAs:As has been used as a photoconductive switch to launch sub-picosecond pulses.[9,10] GaAs-based PiN photodiodes with reasonable room-temperature responsivity out to 1.7 μm have been demonstrated by incorporating GaAs:As as the *i* layer.[11] This responsivity is due to internal photoemission from the As clusters.[12]

We have recently observed an unexpectedly large room-temperature electro-optic effect in GaAs:As and AlGaAs:As due to confinement of excitons in the semiconductor regions between the As clusters.[13] This electo-optic effect is strongly affected by the spacing of the As clusters. In this article we describe how the As cluster spacing is controlled with the coarsening anneal and the subsequent electro-optic properties observed in AlGaAs:As.

II. DEVICE FABRICATION

The film used in this work was grown in a Varian GEN II MBE system. First a 0.5 μm GaAs layer, a 50 nm AlAs layer, and a 20 nm GaAs layer were grown at normal substrate temperatures. The growth was interrupted and the substrate temperature was lowered. A 1 μm thick $Al_{0.25}Ga_{0.75}As$ layer was grown which contained an As excess of 0.18%. The purpose of the 50 nm AlAs layer was to act as a release layer for removal of the 1 μm thick $Al_{0.25}Ga_{0.75}As$ epilayer.

After film growth the sample was cleaved into pieces. The pieces were annealed at temperatures ranging from 650 to 950 °C for 30 s. The anneals were performed in an AG Associates Mini-Pulse rapid thermal processor and for all anneals a ramp rate of 200 °C/s was used. At each temperature two samples were annealed. On one sample at each temperature anneal, transmission electron microscopy (TEM) was performed to determine the average size and density of the As clusters. The second sample at each temperature anneal was prepared for electro-optic characterization. This consisted of epitaxial liftoff of the $Al_{0.25}Ga_{0.75}As$:As epilayer[14] followed by bonding of the $Al_{0.25}Ga_{0.75}As$:As epilayer to a transparent glass slide.[15] Au contacts were deposited on the epilayer so an electric field could be applied parallel to the film growth direction. The spacing between the Au electrodes is 1 mm.

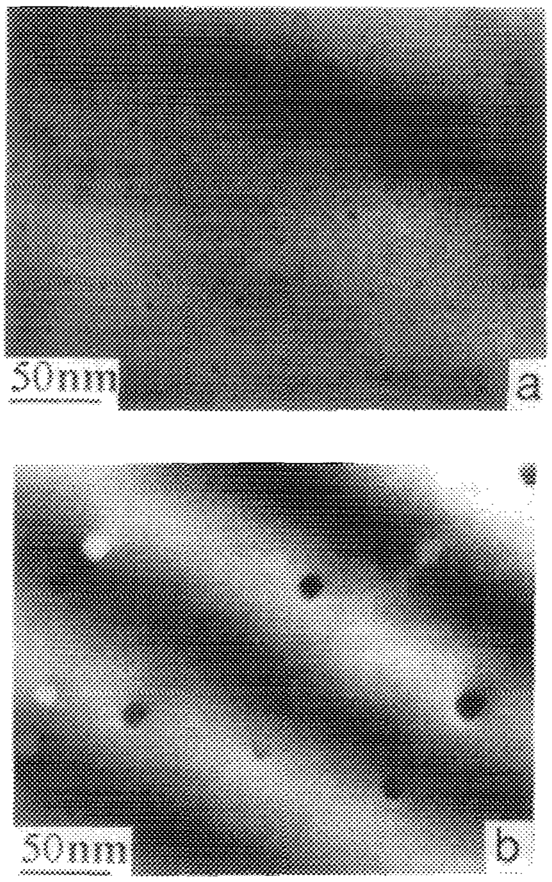

FIG. 1. Transmission electron microscope image of AlGaAs:As after a 30 s anneal at (a) 650 °C and (b) 900 °C. The samples were prepared by ion milling and are wedge shaped. Therefore the thickness contours, which are especially evident in (b) are due to the dynamic diffraction effect (see Ref. 4).

III. DEVICE CHARACTERIZATION

The samples were examined by cross-sectional TEM using a model JEM 2000 EX electron microscope. Shown in Figs. 1(a) and 1(b) are the TEM images of the samples annealed at 650 and 900 °C respectively for 30 s. Clearly seen in Fig. 1 is that as the anneal temperature increases the average size of the As clusters increases while the cluster density decreases. The results of the TEM study of all the samples are displayed in Table I and Fig. 2. The amount of As in clusters for anneal temperatures of 700 °C and above is about 0.18%. The amount of As in clusters at

TABLE I. As cluster coarsening as a function of temperature for 30 s isochronal anneals.

Anneal temperature (°C)	Average cluster diameter (nm)	Average cluster spacing (nm)	Cluster density ($\times 10^{15}$ cm^{-3})	Cluster volume fraction (%)
650	4.7	40	15.6	0.08
700	7.9	52.3	7.0	0.18
750	8.8	60.4	4.54	0.16
800	10.5	72.4	2.64	0.16
900	13.8	88.5	1.44	0.19

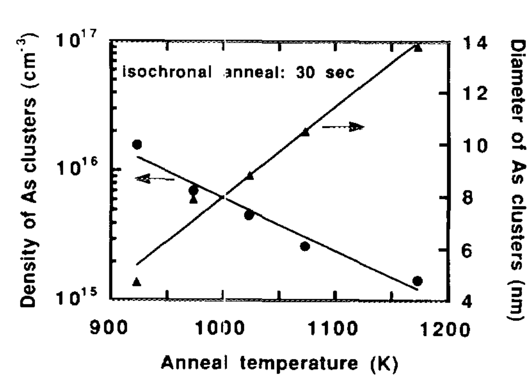

FIG. 2. As cluster average size and density as a function of coarsening anneal. An exponetial curve fit is displayed for the As cluster densities and a linear curve fit for the As cluster diameters.

the anneal temperature of 650 °C is lower at 0.08%. One reason for this lower amount of As in clusters is that the anneal time of 30 s may not be long enough to reach the end of the As cluster growth stage for a temperature of 650 °C. In addition, there is more error in the estimation of the volume fraction of As in clusters at this lower anneal temperature. This is due to the small size of the As clusters that makes it more difficult to get a good estimate of their diameters.

We have previously shown that the volume fraction of excess As is a function of the substrate temperature during growth.[2] Therefore, a combination of the substrate growth temperature and the time and duration of the coarsening anneal will allow one to control both the final average size and density of the As clusters.

The electro-optics were examined by measuring transmission through the 1 μm thick $Al_{0.25}Ga_{0.75}As$:As samples with and without an applied electric field. Shown in Fig. 3 is the band-edge absorption as a function of applied field for the sample annealed at 700 °C. Shown in Fig. 4 is the resulting differential transmission for an applied electric field of 10 kV/cm for the samples annealed at 650, 750, and 900 °C. In Fig. 4 the differential transmission is maximum for the anneal temperature of 750 °C, when the As cluster center-to-center spacing is around 60 nm. The differential

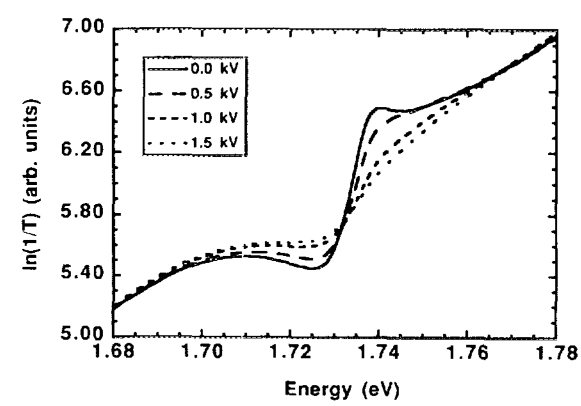

FIG. 3. Band-edge absorption as a function of applied bias for AlGaAs:As containing 0.18% excess As and after a 700 °C 30 s coarsening anneal.

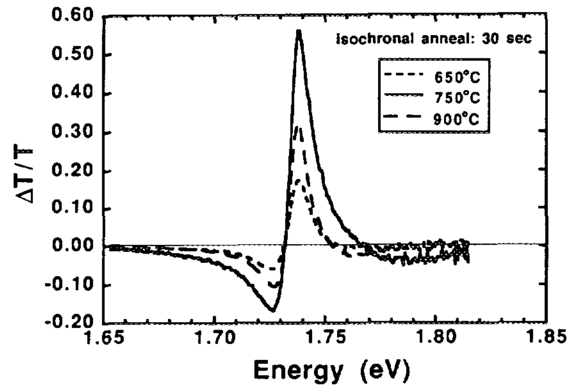

FIG. 4. differential transmission as a function of coarsening anneal for AlGaAs:As using an electric field of 10 kV/cm.

transmission decreases for larger or smaller As cluster spacings.

For the sample annealed at 750 °C, a differential transmission of almost 60% was obtained for an electric field of 10 kV/cm. In addition, the width of the differential transmission in Fig. 4 has a much broader bandwidth than that obtained in GaAs/AlGaAs multiple quantum well structures. This broader bandwidth is due to the inhomogeneity in the AlGaAs:As. This makes AlGaAs:As well suited as a spatial light modulator for broader bandwidth optical signals such as high-speed laser pulses.

As mentioned above, the electro-optic properties of $Al_{0.25}Ga_{0.75}As$:As are optimum when the As cluster center-to-center spacing is around 60 nm. The diameter of the exciton in $Al_{0.25}GA_{0.75}As$ is about 15 nm. When the As cluster spacing is on this order or shorter, the clusters can disrupt the exciton. As the spacing increases, the exciton can be "contained" between the clusters leading to an enhanced electro-optic effect, exhibiting an optimum when the As cluster spacing is about 60 nm. One can think of the exciton as being in a cage formed by the As clusters. As the cluster spacing increases well past the width of the exciton, the enhancement is lost as the material looks increasingly like stoichiometric $Al_{0.25}GA_{0.75}As$ to the exciton. The exact mechanism for the enhancement is still under investigation.

IV. SUMMARY

We have observed an unexpectedly large room-temperature electro-optic effect in AlGaAs:As due to quantum confinement of excitons in the semiconductor regions between the As clusters. The room-temperature band-edge absorption of AlGaAs:As exhibits a clearly defined excitonic edge. This band-edge absorption can be greatly affected by electric field due to exciton lifetime broadening, resulting in almost a 60% differential transmission for a 1 μm thick $Al_{0.25}Ga_{0.75}$:As epilayer. This is comparable to values obtained using GaAs/AlGaAs multiple quantum well structures. The excitonic absorption is a strong function of the average precipitate spacing that we control with the coarsening anneal. This enhancement of the excitonic optical properties by embedded metallic clusters represents a fundamental departure from traditional quantum well engineering.

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