Role of excess As in low-temperature-grown GaAs

A. C. Warren, J. M. Woodall, and P. D. Kirchner
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598

X. Yin and F. Pollak
Department of Physics, Brooklyn College of the City University of New York, Brooklyn, New York 11210

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

N. Otsuka and K. Mahalingam
School of Materials Engineering, Purdue University, West Lafayette, Indiana 47907
(Received 4 December 1991)

Before annealing, low-temperature-grown GaAs contains excess As which is distributed throughout the bulk in the form of point defects that clearly dominate the material's electronic properties. Upon annealing at 600 °C, however, As precipitates are formed which can be readily observed by use of transmission electron microscopy. There has been considerable debate as to whether the electronic properties of the annealed material are controlled by these precipitates, or by residual point defects remaining in the surrounding GaAs. In this paper, we review the relevant data and issues regarding the mechanisms of point-defect-mediated compensation versus the As-precipitate, internal-Schottky-barrier model. In addition, we present data from rapid-thermal-annealing studies of the resistivity-versus-precipitate distribution, and from electromodulation measurements of Fermi-level positions in as-grown and annealed material on both n^+- and p^+-type substrates. These and existing data confirm that the controlling mechanism in the annealed material (GaAs:As) is indeed that of Schottky-barrier-controlled internal pinning on metallic As precipitates.

GaAs grown at 200–250 °C and subsequently annealed at 600 °C has proven valuable in both electronic and optoelectronic applications, but the source of its extremely high resistivity has been the subject of some debate.[1–4] A variety of characterization techniques were applied to both the as-grown and annealed layers, with several interesting results. As-grown material [low-temperature (LT) GaAs] was found to be highly strained, containing roughly 1–2 % excess As and as high as $10^{20}/cm^3$ As-antisite defects [by electron paramagnetic resonance (EPR)],[5,6] with essentially no photoluminescence response.[7] The balance of the excess As is most likely distributed as interstitials, contributing to the strain. While the excess As remained after anneal, the strain and point defects were eliminated (to resolution limits),[6] and a fast photoluminescence response could now be observed.[7]

The change in material properties upon annealing was not understood until it was found that a substantial fraction of the excess As in the material actually precipitated out into macroscopic As clusters.[6,8,9] A 600 °C anneal was found to result in irregular precipitates, with roughly 6 nm diameter and a volume density of $10^{17}/cm^3$, which, within experimental error, accounts for all the excess As.[6,9] This corroborated the observations by EPR that defect densities were reduced from above 10^{19} to below the resolution limit of about 10^{18} cm^3. In addition, the photoresponse is consistent with the starting, heavily defected LT GaAs being converted into a high-quality, optically active GaAs matrix, with embedded As precipitates (GaAs:As) which act as sparse recombination centers for photogenerated carriers. This was used to advantage in the fabrication of terahertz-speed transceivers using GaAs:As as the photoactive material, which demonstrated turn-on speeds indistinguishable from that of bulk GaAs.[10]

With the observation of As precipitates in annealed LT GaAs, Warren *et al.* proposed a simple model for its electronic properties,[1] which assumed that the observed As precipitates were metallic, and that the Schottky-barrier height of As to GaAs held. In this model, As precipitates would be surrounded by depletion spheres in heavily doped material, or completely deplete more lightly doped GaAs, regardless of dopant carrier *type*. The principal alternative model is defect-mediated pinning by a deep donor as observed in unannealed LT GaAs.[2–4] In this paper, we review the electronic properties of GaAs:As in light of these two models, and present further measurements of the dependence of sample resistivity on precipitate distribution, and of band bending and Fermi-level-pinning position in heterostructures containing undoped GaAs:As. These data are shown to fit the simple Schottky model, and are inconsistent with a defect-mediated Fermi level in this system.

A prediction of the precipitate Schottky model is that there should be a clear relationship between doping, precipitate densities, and conductivity. When the doping density is high enough, or the precipitate density low enough, individual precipitates will be surrounded by iso-

lated depletion spheres, which leave the material only partly compensated and therefore conducting. In the converse, the depletion regions overlap so that there are no free carriers and the material is semi-insulating. It has been observed that rapid thermal annealing (RTA) of a doped but previously nonconducting sample could be made conductive, or "activated."[11] Within our model, this could be explained if the excess As were being redistributed through precipitate "coarsening," which is driven by the tendency of the system to reduce its precipitate/matrix interfacial area.[12] To study this, *n*- and *p*-type wafers of several doping densities were grown, using our standard LT GaAs plus 600 °C cap technique. Samples were then exposed to various RTA cycles and examined using cross-section transmission electron microscopy (TEM) and Hall conductivity measurement of carrier densities and mobilities. Table I shows results from such measurements using *n*-type samples with nominal doping levels of 1×10^{18} and $5\times10^{18}/\text{cm}^3$ and exposed to a 30-sec RTA cycle at 700, 800, or 900 °C. Statistical means for precipitate diameter and volume density were extracted from the TEM measurements, and confirm that the RTA is indeed causing a coarsening of the As distribution in favor of sparse, large precipitates.

The RTA "activation" of these doped samples is completely consistent with the observed precipitate coarsening, resulting in isolated "depletion spheres" which are decreasingly effective in compensating the doped GaAs. A simple calculation of Laplace's equation for an isolated precipitate can be used to estimate the amount of charge on it, and therefore the amount of doping a precipitate could compensate. For example, a barrier height of 0.7 eV would result in about 18 excess electrons charge (on a 6 nm precipitate), so that $10^{17}/\text{cm}^3$ precipitates could compensate up to $2.3\times10^{18}/\text{cm}^3$ doping. Assuming uniform doping, this model gives a precipitate-size/conduction threshold of 5 nm for $5\times10^{18}/\text{cm}^3$ material, and 12 nm for 1×10^{18}, in agreement with the measured data in Table I. The heavily doped samples do not fully activate, as could be expected if the doping concentration in the GaAs were correllated with the As precipitate location. This is consistent with measurements of impurity redistribution in heavily Si-doped, arsenic-rich LT-grown GaAs during high-temperature anneals.[13]

In order to probe the electric fields in and adjacent to LT-grown layers, special heterostructure stacks were grown for electromodulation (EM) measurements. Here, n^+ (N) and p^+ (P) buffer layers (doped at $5\times10^{18}/\text{cm}^3$) were grown on like substrates, followed by a 50-nm undoped (U) GaAs *i* layer at 600 °C. At this point, the temperature was dropped to 250 °C and 150 nm of LT GaAs was deposited for samples referred to as LTUN and LTUP, respectively. In other samples, this recipe was followed by an *in situ* ramp back up to 600 °C, followed by a 20-nm cap of undoped GaAs and 1-h anneal at 600 °C in an As_2 flux. These samples are referred to as ALTUN and ALTUP layers. Electric fields in these samples were then measured from the Franz-Keldysh oscillations (FKO's) observed using both photoreflectance (PR) (Ref. 14) and contactless electroreflectance (CER).[15] These two techniques gave identical fields; in addition, CER gave the field sign from the phase of the reflected signal. In the LTUN structure, the measured field was 1.1×10^5 V/cm, which corresponds to the built-in field at the *i*-layer/n^+ interface. This value places an upper limit of about 0.5 eV for the Fermi-level distance from the conduction-band edge at the LT/*i*-layer interface. In the LTUP sample, the measured field was 1.8×10^5 V/cm, which corresponds to a Fermi-level position in the LT material of around 0.4–0.5 eV below the conduction band. These two measurements are exactly what one would expect from a single deep donor level 0.4 eV below the conduction band, which corresponds to the EPR (Ref. 3) and infrared-absorption[16] measured As-antisite defect. Figure 1 shows our modeling results for the LTUN case with such a defect, illustrating the lack of firm pinning for this system.

Data from the ALTUN and ALTUP samples, however, indicate a completely different system. The measured field in both samples was 1.25×10^5 V/cm, indicate a single midgap GaAs:As Fermi-level position for both samples. Allowing for doping degeneracy and Debye tailing in the doped substrates, and an 8-nm Debye tail in the GaAs:As layer, our calculations yield equal fields of 1.3×10^5 V/cm, with a pinning position of 0.67 eV below the conduction-band edge. Modeling of the band bending for the ALTUN case is shown in Fig. 2, showing the extreme contrast between this case and the LTUN (unannealed) one. The extrapolated pinning position is in excellent agreement with our measured Fowler-Nordheim

TABLE I. TEM and Hall data for as-grown and annealed (600 °C), and rapid thermal annealing samples (700, 800, and 900 °C). Top group is mean precipitate size and distribution data, while lower two groups are electron density and mobility for bulk doping levels of 1 and $5\times10^{18}/\text{cm}^3$.

	600	700	800	900
Diameter (nm)	5.5	7	15	20
Spacing (nm)	18	22.5	47.5	67.5
N_D ($\times10^{15}$ cm^{-3})	170	87	9.3	3.2
Volume fraction	0.015	0.016	0.016	0.014
$n_{1\times10^{18}}$ ($\times10^{17}$ cm^{-3})		0.003	4	5
$\mu_{1\times10^{18}}$ (cm^2/V s)		420	1520	1950
$n_{5\times10^{18}}$ ($\times10^{17}$ cm^{-3})		1.2	7.5	11
$\mu_{5\times10^{18}}$ (cm^2/V s)		680	1180	1320

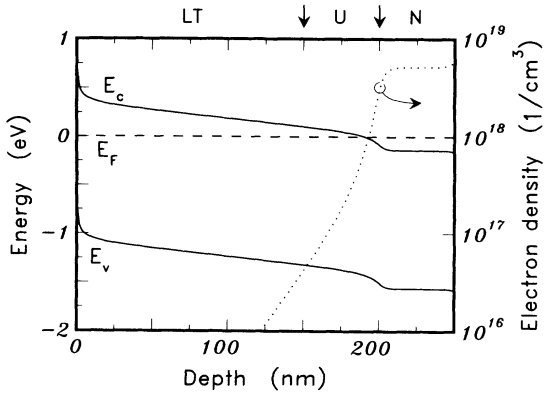

FIG. 1. Band-bending diagram for LTUN (unannealed) structure. A deep donor is included in the LT material with energy 0.4 eV below the conduction-band edge. Arrows indicate the interface between the LT, U, and N layers.

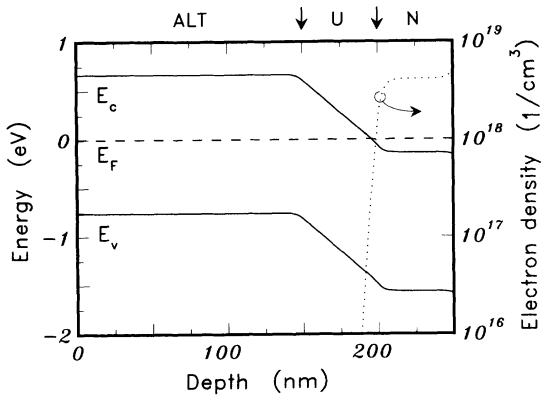

FIG. 2. Band-bending diagram for ALTUN (annealed) structure. The Fermi level in the ALT material is pinned at 0.67 eV below the conduction-band edge (E_c) and includes a Debye tail of 9 nm at the ALT/U interface. Arrows indicate the interface between the ALT, U, and N layers.

photoresponse threshold of 0.7 eV,[17] and is what one would expect from the barrier height of As to GaAs. In addition, it is clear that such pinning could not be produced by a single donor or acceptor defect.

The defect-mediated compensation model is hard pressed to explain the available data. First, both donor and acceptor levels at the same energy, and with densities greater than mid $10^{18}/cm^3$, would be required to explain the ALT material's observed doping compensation. Second, these levels would have to have been created during the 600 °C anneal, as they are not evident in the LT material. Third, in contrast to the *EL*2 level in LT GaAs, these defects must be invisible to EPR and yield no discrete DLTS signal.[11] Fourth, they can have only negligible effect on carrier mobilities as found in THz optoelectronic transceivers. Fifth, while being created by the 600 °C anneal, they must be gradually removed by higher temperature RTA's in order to produce the observed doping "activation." And finally, these defects must be relatively transparent in the infrared, as early results clearly show the discrete level associated with *EL*2 being removed by annealing at 600 °C leaving a uniform, clean GaAs background.[6,11] To our knowledge, there are no defects in GaAs that fulfill these criteria. And while it is certainly probable that some low level of residual point defects in the GaAs matrix remain, their density is below the resolution limit of available detection methods, and they cannot explain the observed optical and electronic properties.

In conclusion, we have presented new measurements of carrier compensation and band bending in GaAs:As, and shown that these data are consistent with our model of Schottky pinning at As precipitates formed during a 600 °C anneal. Examination of these and prior data shows that the electronic properties of this system are clearly inconsistent with a defect-controlled model. While it is possible that earlier reports were misled through the examination of incompletely annealed samples, our results indicate that the electronic properties of LT GaAs annealed at 600 °C or above are completely controlled by the Schottky barriers between the resulting As precipitates and the surrounding GaAs.

We would like to acknowledge the assistance of J. De Gelormo and D. McInturff with the RTA experiments, and X. Guo in taking PR and ER measurements. Thanks also to T. Jackson for numerous helpful discussions. X.Y. and F.H.P. acknowledge the support of the New York State Science and Technology Foundation through its Centers for Advanced Tech. Program, the Olympus Corp. and PSC/BHE.

[1]A. C. Warren, J. M. Woodall, J. L. Freeouf, D. Grischkowsky, D. T. McInturff, M. R. Melloch, and N. Otsuka, Appl. Phys. Lett. **57**, 1331 (1990).

[2]F. W. Smith, H. Q. Le, V. Diadiuk, M. A. Hollis, A. R. Calawa, S. Gupta, M. Frankel, D. R. Dykaar, G. A. Moureau, and T. Y. Hsiang, Appl. Phys. Lett. **54**, 890 (1989).

[3]M. Kaminska, Z. Liliental-Weber, E. R. Weber, T. George, J. B. Kortright, F. W. Smith, B-Y. Tsaur, and A. R. Calawa, Appl. Phys. Lett. **54**, 1881 (1989).

[4]M. O. Manasreh, D. C. Look, K. R. Evans, and C. E. Stutz, Phys. Rev. B **41**, 10272 (1990).

[5]M. Kaminska, E. R. Weber, Z. Liliental-Weber, and R. Leon, Vac. Sci. Technol. B **7**, 710 (1989).

[6]Z. Liliental-Weber, G. Cooper, R. Mariella, and C. Kocot, Vac. Sci. Technol. B **9**, 2323 (1991).

[7]Jeff Kash (private communication).

[8]M. R. Melloch, N. Otsuka, J. M. Woodall, A. C. Warren, and J. L. Freeouf, Appl. Phys. Lett. **57**, 1531 (1990).

[9]K. Mahalingam, N. Otsuka, M. R. Melloch, J. M. Woodall, and A. C. Warren, Vac. Sci. Technol. B **9**, 2328 (1991).

[10]A. C. Warren, N. Katzenellenbogen, D. Grischkowsky, J. M. Woodall, M. R. Melloch, and N. Otsuka, Appl. Phys. Lett. **58**, 1512 (1991).

[11]W. J. Schaff (unpublished).

[12]P. W. Voorhees, J. Stat. Phys. **38**, 231 (1985).

[13]K. Kavanaugh and P. D. Kirchner (private communication).

[14]X. Yin, H-M. Chen, F. H. Pollak, P. A. Montano, P. D. Kirchner, G. D. Pettit, and J. M. Woodall, Appl. Phys. Lett. **58**, 260 (1991).
[15]X. Yin and F. Pollak, Appl. Phys. Lett. **59**, 2305 (1991).
[16]D. C. Look, D. C. Walters, M. O. Manasreh, J. R. Sizelov, C. E. Stutz, and K. R. Evans, Phys. Rev. B **42**, 3578 (1990).
[17]D. T. McInturff, J. M. Woodall, A. C. Warren, N. Braslau, G. D. Pettit, P. D. Kirchner, and M. R. Melloch, Appl. Phys. Lett. **60**, 448 (1992).