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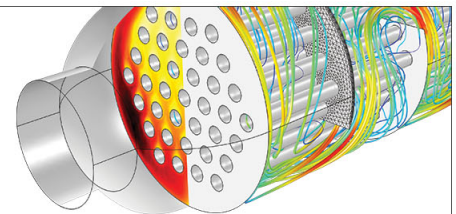
The compensation and depletion behavior of iron doped GaAs grown by molecular beam epitaxy

D. T. McInturff,[a)] E. S. Harmon, J. C. P. Chang, T. M. Pekarek,[b)] and J. M. Woodall
School of Electrical and Computer Engineering and the MRSEC for Technology Enabling Heterostructure Materials, Purdue University, West Lafayette, Indiana 47907

We describe the growth and characterization of GaAs films in which a high concentration (1 at. %) of elemental iron is introduced during growth in a conventional molecular beam epitaxy system. For films grown at 600 °C, the iron incorporates as Fe_3GaAs precipitates. Unlike the formation of As precipitates in low temperature grown (LTG) GaAs, iron precipitate formation does not require a postgrowth anneal. Hall measurements of the as-grown $GaAs/Fe_3GaAs$ composite intentionally doped with silicon indicate that Fe_3GaAs precipitates will deplete carriers in the same manner as As precipitates deplete carriers in annealed LTG GaAs. The degree of depletion depends on the initial growth temperature and the intentional doping level. Electrical behavior of samples subjected to a postgrowth rapid thermal anneal indicate that the material is deep level compensated by iron acceptor doping via dissolution of the Fe_3GaAs precipitates. © *1996 American Institute of Physics.* [S0003-6951(96)00339-7]

GaAs that has been grown at low (200 °C–250 °C) temperature and then annealed at >600 °C (GaAs:As) has been found to contain a high density of arsenic precipitates.[1] Many interesting features of this new material, such as a high resistivity and sensitivity to subbandgap light, have been explained in terms of buried precipitates acting as internal Schottky barriers.[2–7] In the GaAs:As system it was discovered by Warren *et al.* that there was a relationship between the arsenic precipitate density, which is controlled by anneal conditions, and conductivity.[2] That study was instrumental in identifying depletion by buried Schottky barriers as the mechanism by which arsenic precipitates render GaAs:As semi-insulating. Qualitatively, the higher the anneal temperature, the more arsenic would ''ripen'' into a smaller number of larger arsenic precipitates. This behavior was observed directly by transmission electron microscopy (TEM),[1] and was later correlated with the results from transport studies.[2,3] As the precipitate density was reduced in favor of larger precipitates, the conductivity of intentionally doped samples was increased since the depletion regions surrounding each precipitate could no longer deplete the entire volume of the sample. While a study of transport properties alone cannot fully characterize a new composite material, it is possible to infer a great deal of information beyond just how the composite will behave electrically by comparing the behavior of the new composite to GaAs:As. Thus, it is worthwhile to revisit the study by Warren *et al.* when studying new composite systems.

It is known that an iron/GaAs composite can be formed via implantation and by molecular beam epitaxy (MBE).[8,9] In the case of the implantation study, the precipitate has been identified as Fe_3GaAs.[9] Preliminary studies of the implanted material also indicate that qualitatively over some range of anneal conditions the buried precipitates deplete the GaAs host in a manner analogous to GaAs:As.[9] Qualitatively, it is not expected that GaAs:Fe will behave exactly as GaAs:As. For one thing, iron is known to act as a *p*-dopant in GaAs with a solubility as high as $3 \times 10^{17}/cm^3$ in GaAs when annealed at 950 °C.[9] Also, unlike the case for arsenic precipitates in GaAs, the Schottky barrier behavior of Fe_3GaAs precipitates is not known, i.e., whether they will deplete and/or compensate *n*- and *p*-type GaAs equally. Finally, there are only very sparse data on how precipitate density and size can be controlled.

In order to study some of these properties via transport measurements, GaAs:Fe films were grown on semi-insulating GaAs substrates in a Gen II MBE system equipped with a high temperature iron effusion cell charged with 99.999% pure elemental iron. Each of the Fe-doped films, except for the GaAs:Fe sample used in a transmission electron microscopy (TEM) study, were double heterostructures (DH) with a 1 μm thick GaAs:Fe layer sandwiched between two $Al_{0.3}Ga_{0.7}As$ layers. The iron cell temperature was set to maximize the amount of iron that was incorporated into the GaAs layers without causing a spotty electron diffraction pattern (RHEED). The iron was codeposited with the GaAs and the layers were grown at the standard MBE growth temperature of 600 °C. RHEED was performed at various points throughout the growths. Streaky RHEED patters were consistently observed throughout the growth of the GaAs:Fe layers indicating smooth two-dimensional growth. Upon removal from the MBE system, all samples appeared to be shiny and smooth.

Iron content in these experiments was established by correlating a beam equivalent pressure measurement with a TEM measurement. The TEM was performed in order to establish the presence, size, and density of the Fe_3GaAs precipitates. All subsequent estimates of iron content were made by comparing beam equivalent pressures. Figure 1 shows a TEM of a sample containing iron precipitates. The GaAs surrounding the precipitates was of good quality and was free of defects. From diffraction patterns, we conclude that the precipitates in this study are also composed of

[a)]Electronic mail: mcntrff@ecn.purdue.edu
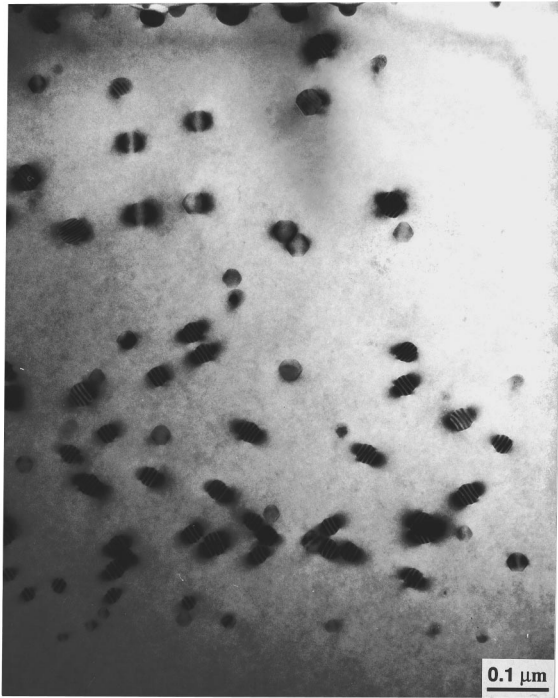[b)]Department of Physics, Purdue University, West Lafayette, IN 47907.

FIG. 1. Transmission electron microscope image of GaAs/Fe₃GaAs composite. Fe₃GaAs clusters are 40 nm in diameter and have a density of 2.5 $\times 10^{14}$/cm³. Iron concentration is approximately 1 at. %.
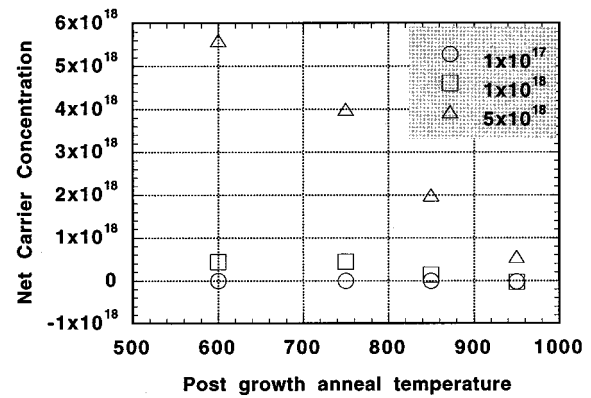

FIG. 2. Plot of postgrowth anneal temperature vs net carrier concentration in GaAs:Fe samples that have been intentionally doped with silicon. The legend indicates the intentional silicon doping concentration. In this plot an *n*-type carrier concentration is assigned a positive value on the vertical axis. Several samples became lightly *p*-type at higher anneal temperatures, which is indicated by a negative value for net doping concentration. Data corresponding to a 600 °C postgrowth anneal is for as-grown samples.

Fe₃GaAs.[9] These precipitates are 40 nm in diameter. The Fe₃GaAs precipitate density was roughly 2.5×10^{14}/cm³. The Fe₃GaAs precipitates occupy about 0.86% of the volume of the GaAs:Fe epilayer. Assuming a hexagonal structure with $c = 0.523$ nm and $a = 0.422$ nm for Fe₃GaAs, we estimate this to be equivalent to about 1 at. % of iron. In contrast, for low temperature grown GaAs, 2% excess arsenic forms precipitates with diameters of about 5 nm and a density of about 2×10^{17}/cm³ upon anneal at 600 °C.

Similar to the electrical behavior previously observed in the implantation study, an unintentionally doped MBE grown GaAs:Fe sample was too resistive to measure but became *p*-type with a carrier concentration of 1×10^{16}/cm³ upon anneal at 950 °C.[9] To explore the behavior of the composite when dopants are added, three double heterostructure samples were intentionally doped *n* type with silicon to levels of 1×10^{17}/cm³, 1×10^{18}/cm³, and 5×10^{18}/cm³. The results of Van der Pauw measurements performed on these samples are shown in Fig. 2. For the GaAs:Fe as-grown at 600 °C and intentionally doped at 1×10^{17}/cm³, the resistivity was too high for accurate hall measurement indicating a significant level of either depletion or compensation. The sample doped at 1×10^{18}/cm³, however, had a carrier concentration of 4×10^{17}/cm³ and the sample doped at 5×10^{18}/cm³ had a carrier concentration of around 5×10^{18}/cm³. The mobilities of the as-grown GaAs:Fe samples intentionally doped at 1×10^{18}/cm³ and 5×10^{18}/cm³ are 1793 cm²/V s and 938 cm²/V s, respectively, which is roughly half the value of mobilities of similarly doped GaAs that does not contain iron.

The three DH structures were also given rapid thermal anneals at 750 °C, 850 °C, and 950 °C for 30 s. Those results are also in Fig. 2. The sample that was intentionally doped with 1×10^{17}/cm³ silicon turned *p*-type with a carrier concentration of 4×10^{15}/cm³ after an anneal at 850 °C. After an anneal at 950 °C, the sample had a *p*-type carrier concentration of 2×10^{16}/cm³. Thus, in contrast to GaAs:As, where the conductivity increases upon anneal and does not change type, GaAs:Fe appears to compensate upon anneal. For the samples intentionally doped at 1×10^{18}/cm³ and 5×10^{18}/cm³, the apparent compensation upon anneal is even more pronounced. The solubility limit for iron in GaAs after a rapid thermal anneal at 950 °C inferred from the behavior of GaAs:Fe intentionally doped with silicon at 1×10^{17}/cm³ would be about 1.2×10^{17}/cm³, whereas the solubility limit for iron in GaAs intentionally doped at 5×10^{18}/cm³ is about 4.5×10^{18}/cm³. This solubility is the highest reported for iron in GaAs.[11]

There appears to be a dramatic solubility increase with increasing *n*-type doping. It is well known that there is a tendency for a crystal to minimize its total free energy by creating electrically active defects in order to compensate the effect of any intentional dopants,[10] i.e., drive the crystal towards being "intrinsic." This tendency is particularly true for wide band-gap semiconductors such as ZnSe. In the case of the Fe₃GaAs/GaAs composite, the Fe₃GaAs precipitate appears to decompose upon anneal in order to create GaAs plus iron that is in turn free to incorporate as an acceptor dopant, thus, driving *n*-doped material toward intrinsic.

Although the electrical behavior of the *n*-type samples subjected to postgrowth anneals appears to be dominated by compensation caused by iron going to acceptor sites, it is not necessarily the case that the electrical behavior of GaAs:Fe as-grown at 600 °C is due to compensation. For the case of the as-grown GaAs:Fe intentionally doped at 1×10^{17}/cm³, the material is already quite resistive even though the solubility of Fe in GaAs at 600 °C should be below 1×10^{16}/cm³.[11] To clarify this, an additional DH sample with an intentional doping concentration of 1×10^{18}/cm³ was grown with <0.1 at. % (4×10^{20}/cm³) iron. This amount would be sufficient to compensate GaAs:Fe silicon doped at

$1 \times 10^{18}/cm^3$ upon anneal at 900 °C but insufficient to form precipitates large enough or dense enough to deplete the as-grown sample. This sample, as-grown, had a carrier concentration of $1 \times 10^{18}/cm^3$ and was, therefore, unaffected by the addition of iron. Upon anneal at 900 °C, however, the sample had a p-type carrier concentration of $8 \times 10^{15}/cm^3$. Thus, the electrical behavior of the as-grown GaAs:Fe samples in Fig. 2 was controlled by depletion from buried precipitates rather than by compensation.

As noted above, the precipitates in the GaAs:Fe as grown at 600 °C are 40 nm in diameter, which is significantly larger than precipitates typically found in GaAs:As. In the case of GaAs:As, precipitates of that size and corresponding density would be formed by a postgrowth anneal of greater than 900 °C and would only be expected to deplete material intentionally doped n type up to a level of about $3 \times 10^{17}/cm^3$.[2] This is consistent with our observation that the as-grown GaAs:Fe doped at $1 \times 10^{18}/cm^3$ was only partially depleted. For GaAs:As, the volume of host material that is depleted by the precipitate can be increased by making smaller/more dense precipitates, which is accomplished by reducing the postgrowth anneal temperatures. In the case of GaAs:Fe grown by MBE, it would also be desirable, for many applications, to make smaller/more dense precipitates.

In a previous study of MBE grown GaAs:Fe it was observed that iron precipitates with a smaller average diameter of 20 nm and a correspondingly higher density of $1.2 \times 10^{15}/cm^3$ were formed in relatively thin codeposited layers.[8] Although there have been no systematic studies on how to control iron precipitate size and density, this is evidence that such control is possible. Some attempts have been made at growing GaAs:Fe at lower temperatures in order to control the iron surface mobility during growth and, hence, the precipitate size and density. So far, however, material grown at low (400 °C–450 °C) temperature has had very spotty RHEED patterns. Preliminary TEM studies of such material shows that the precipitate diameter in material grown at low temperature does not change significantly from that of Fe_3GaAs precipitates grown in at 600 °C. Although it has been shown that precipitates formed by implantation[9]

can have a size and density that is controllable by postimplant anneal, more study is required to determine the mechanism for that type of control in MBE.

In conclusion, we report the formation of iron/GaAs composites by growth in an MBE system. TEM measurements confirm that GaAs:Fe as grown at 600 °C contains Fe_3GaAs precipitates. Hall measurements of GaAs:Fe samples intentionally doped with silicon reveal that there is much similarity between the behavior of the as-grown Fe_3GaAs/GaAs composite and arsenic precipitates in GaAs. Fe_3GaAs precipitates appear to be responsible for the depletion of as-grown samples that have been intentionally doped n type to a level of about $5 \times 10^{17}/cm^3$. Unlike the case of GaAs:As where precipitates dominate the electrical behavior after high temperature anneals, the electrical behavior of GaAs:Fe is dominated by compensation due to acceptors when subjected to postgrowth anneals of >600 °C. The solubility of the iron is observed to be a strong function of both temperature and intentional doping level.

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