Precipitation in Fe- or Ni-implanted and annealed GaAs

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We report the formation of metal/semiconductor composites by ion implantation of Fe and Ni into GaAs and a subsequent anneal to nucleate clusters. Electron diffraction experiments and high resolution transmission electron microscopy images indicate that these precipitates are probably hexagonal and metallic Fe\textsubscript{3}GaAs or Ni\textsubscript{3}GaAs with orientation relationship to GaAs of (10\textsubscript{1}0)\textsubscript{pp}∥(42\textsubscript{2}2)\textsubscript{m}, (00\textsubscript{2}2)\textsubscript{pp}∥(11\textsubscript{1}1)\textsubscript{m}, and [1\textsubscript{2}1\textsubscript{0}]\textsubscript{pp}∥[011]\textsubscript{m}. Correlation of the electrical and structural properties of the samples annealed at different temperatures shows that the buried Schottky-barrier model has general applicability. © 1994 American Institute of Physics.

Metal-semiconductor composites, such as GaAs:As with small As precipitates dispersed in a GaAs matrix, have demonstrated remarkable electronic and optical properties. GaAs:As can suppress sidegating or backgating in GaAs integrated circuits by providing excellent device isolation.\textsuperscript{1} In addition, this composite exhibits reasonable mobilities and in some cases subpicosecond lifetimes, which make it useful for ultrafast photoconductive switch applications.\textsuperscript{2} GaAs:As has also demonstrated unusual optical properties.\textsuperscript{3} Although some controversy still remains, the optoelectronic properties can be explained by the depletion action of buried Schottky barriers associated with the As precipitates.\textsuperscript{4}

Recent calculations\textsuperscript{5} show that metals can have stronger effects on the dielectric and optical properties of composites, thus making it attractive to search for a substitute to the semimetallic As precipitates in GaAs. A variety of experimental techniques, including molecular beam epitaxy (MBE) growth of GaAs at low temperatures\textsuperscript{6} and ion implantation,\textsuperscript{7} have been employed to fabricate GaAs:As. In this letter we introduce a technique to form composites using ion implantation of the transition metals Fe or Ni into GaAs and a subsequent anneal to nucleate clusters. Transition metals were chosen because they are important in semiconductor technology and they can easily form precipitates in semiconductors,\textsuperscript{8} e.g., Fe\textsubscript{2}As microclusters in Fe grown on GaAs by MBE,\textsuperscript{9} and Fe-containing compounds in GaAs grown on FeGa films,\textsuperscript{10} or in Fe-doped GaAs grown by liquid encapsulation Czochralski.\textsuperscript{11,12} Here we present detailed transmission electron microscopy (TEM) studies and electrical measurements of the novel GaAs:Fe and GaAs:Ni composites.

GaAs samples were implanted with 1×10\textsuperscript{16} ions/cm\textsuperscript{2} of Fe\textsuperscript{1} or Ni\textsuperscript{2} at an energy of 170 keV and at room temperature. TRIM simulations\textsuperscript{13} of final ion distributions indicate a range of 85 nm, a straggler of 45 nm, and a peak concentration of 9×10\textsuperscript{20}/cm\textsuperscript{3}, i.e., ~4 at. % in GaAs. The latter is well above the Fe solubility limit in GaAs at 950 °C~3×10\textsuperscript{17}/cm\textsuperscript{3}. The samples were further annealed in a rapid thermal processor at 950 °C for 30 s or at 600 °C for 30 min with GaAs proximity caps. The (011) cross-sectional transmission electron microscopy (XTEM) specimens were prepared by standard ion milling and then observed with a Jeol 2000 EX electron microscope. Scanning electron microscopy (SEM) examination was performed on a Jeol JSM-35CF.

The (004) x-ray rocking curve of the as-implanted samples had an extra peak observed towards smaller angles, indicating an expansion in the lattice in the implanted region. After annealing only a sharp substrate peak with FWHM of 14 arcsec was seen. This suggests that most of the strain in the GaAs matrix was relaxed by precipitation, which was also verified by TEM. TEM analysis of the annealed material revealed a composite structure consisting of metal clusters in a GaAs matrix. Figure 1 is a bright-field XTEM image for the Fe-implanted sample that was annealed at 950 °C for 30 s. End-of-range damage in the form of dislocation loops (marked “dl”) is present at a depth of 170–600 nm below the surface. From the surface to a depth of about 170 nm, precipitates of different sizes are found to be surrounded by a GaAs crystal. The size of a typical precipitate (marked “p”) is 35 nm in diameter with moiré fringes clearly seen. The

![FIG. 1. Bright-field TEM image of a GaAs region that was implanted with Fe and annealed for 30 s at 950 °C. Precipitates (p) highlighted with moiré fringes and dislocation loops (dl) are observed at different depths below the surface. Similar results hold for the Ni-implanted GaAs.](image-url)
Fe-implanted sample along a [111] GaAs. One example is shown in Fig. 2 for the specimen tilting. In the SADP, weak spots appear in addition to the spots of GaAs obtained by analyzing from three different zone axes of GaAs. Of these only FeAs can fit the patterns along the [101] and [002] directions. The latter is more likely as shown by high resolution TEM (HRTEM) images. Figure 3 is the HRTEM image of the precipitate (marked p in Fig. 1) after rethinning with part of the GaAs matrix milled away. Regions without severe damage clearly show orthogonal lattice fringes with spacings of 0.35 and 0.50 nm, corresponding to the (101) and (0001) planes of Fe₃Ga₃As, respectively. The (0002) lattice images appear weaker than the (0001) superstructure lattice images. The doubling of the (0002) fringes as well as the superspots in the diffraction pattern indicate the occurrence of ordering in the precipitate. To our knowledge no ordering has been reported with FeAs. The Fe₃Ga₃As alloys, which can exist over a range of composition, undergo a change in structure to more ordered variants with increasing gallium content at x ≈ 0.85. This change is consistent with ordering of vacancies in the Fe sites. Another difference between these two candidate crystals is that FeAs is antiferromagnetic and Fe₃Ga₃As is ferromagnetic. Magnetic measurements may offer clues to the phase identification.

As in the case for GaAs:As, the average size and corresponding density of the Fe₃Ga₃As precipitates can be controlled by the temperature and duration of the anneal. Figure 4 is a [011] HRTEM image showing the 140 ± 20 nm regrown layer of the Fe-implanted sample that was annealed at 600 °C for 30 min. Small round-shaped precipitates (3–5 nm in diameter) are seen homogeneously distributed in GaAs from the depth of 40 nm throughout the entire regrown layer. The average separation between these precipitates is about 3 nm. From the surface to the depth of 40 nm, larger precipitates (6–7 nm) highlighted with moiré fringes appear to accumulate underneath the surface without protruding the surface as seen in the sample annealed at 950 °C. These observations agree with the reported Fe outdiffusion in other Fe-implanted GaAs using secondary-ion-mass spectroscopy.

The Ni samples look very similar to the Fe samples under both the image and diffraction modes of TEM. It is rea-
reasonable to assume that the precipitates in these two samples have the same structure. Unlike FeAs, NiAs is hexagonal and it cannot explain the diffraction pattern. The diffraction pattern was therefore identified as being due to a hexagonal Ni$_3$GaAs (\(a=0.39\), and \(c=0.501\) nm) with an orientation relationship given by \((1010)_{pp}\parallel(422)_{m}\), \((0002)_{pp}\parallel(111)_{m}\), and \([1210]_{pp}\parallel[110]_{m}\). Nearly perfect lattice match between the \((1010)_{pp}\) and the projection of \((002)_{pp}\) on \((111)_{m}\) leads to the formation of facets along \((111)_{m}\). The doubling of the \((0002)\) fringes as well as the superspots in the diffraction pattern indicates the occurrence of ordering in the precipitate. The sizes and densities of the precipitates can be controlled by the annealing temperatures. Correlation of the electrical and structural properties of the samples at different temperatures indicate that the buried Schottky-barrier model has general applicability. The ability to form these composites with different metals may allow an additional degree of control of the composite properties.

FIG. 4. [011] HRTEM image of the Fe-implanted GaAs that was annealed at 600 °C for 30 min showing the presence of precipitates (arrowed) within the GaAs matrix. Similar results hold for the Ni-implanted GaAs.

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