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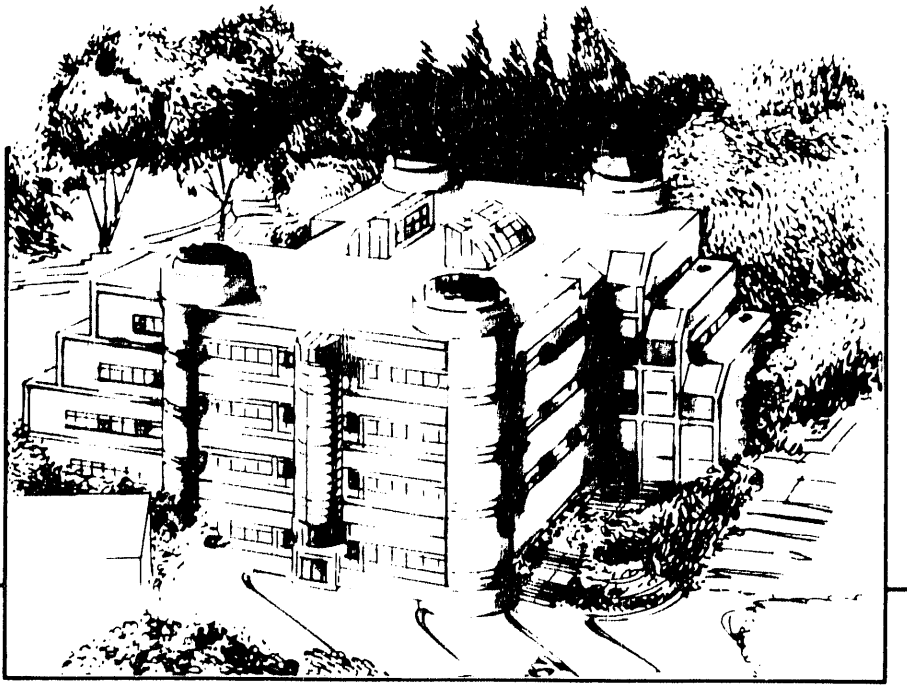

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THE EFFECT OF CO-IMPLANTATION ON THE ELECTRICAL ACTIVITY OF IMPLANTED CARBON IN GaAs

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ABSTRACT

We have undertaken a systematic study of the effect of co-implantation on the electrical properties of C implanted in GaAs. Two effects have been studied, the additional damage caused by co-implantation and the stoichiometry in the implanted layer. A series of co-implant ions were used: group III (B, Al, Ga), group V (N, P, As) and noble gases (Ar, Kr). Co-implantation of ions which create an amorphous layer was found to increase the electrical activity of C. Once damage was created, maintaining stoichiometric balance by co-implantation of a group III further increased the fraction of electrically active carbon impurities. Co-implantation of Ga and rapid thermal annealing at 950°C for 10 s resulted in carbon activation as high as 68%, the highest value ever reported.

INTRODUCTION

Carbon is a particularly attractive shallow acceptor in GaAs since its diffusion coefficient is several orders of magnitude lower than that of group II acceptors such as Be, Mg, or Zn.[1,2] It is not possible to attain abrupt doping profiles with group II acceptors. Graded dopant profiles lead to the degradation of electrical characteristics particularly in heterojunction bipolar transistors (HBT's) which require a thin, heavily doped p-type base layer.[3]

Carbon has also been generating renewed interest as an acceptor in GaAs because of recent successes in growing epitaxial layers with ultra-high carbon concentrations. Layers of GaAs doped with C with free carrier concentrations exceeding 10^{20} cm^{-3} have been attained with growth by MOMBE[4] and MOVPE.[5] Renewed interest in C-doping of GaAs has led to this investigation of ion implantation of C.

Initial attempts at implantation of C in GaAs yielded poor results. C implanted at low doses ($<10^{13}$ cm^{-2}) and fairly high energies (80 - 120 keV) resulted in free carrier concentrations corresponding to nearly 50% of the implanted C atoms becoming electrically active.[6,7] However at doses above 5×10^{13} cm^{-2} (at energies from 20 - 200 keV) activation efficiencies were typically <5%.[8,9] Co-implantation of Ga has resulted in improved activation of implanted C particularly at high doses. Shin et.al.[10] found that co-implantation of Ga increased the electrical efficiency of C from 9% to 32% for C implanted at 60 keV at a dose of 10^{14} cm^{-2} after annealing at 900°C. Dramatic differences due to Ga co-implantation in the electrical characteristics of C implanted layers were seen by Pearton and Abernathy.[11] Activation efficiencies increased from 34% to 60% for 1×10^{13} cm^{-2} implants and from 2.5% to 43% for 5×10^{14} cm^{-2}, 40 keV implants after annealing at 800°C.

The precise role of the Ga co-implant regarding C acceptor activation is unknown. Long range order in the crystal is preserved following the implantation of C (atomic mass = 12 amu). However, the higher mass of the Ga (69-71 amu) and the higher energy at which it is implanted will cause considerable damage to the substrate, thus creating an amorphous layer. The ability of the implanted C to sit on an As site and contribute a free hole may depend on the degree of disorder in the lattice. C doping during epitaxial growth has been highly successful (as mentioned previously) indicating a natural tendency for C to sit on an As site. The solid phase epitaxy (during thermal annealing) of the amorphous layer created by Ga implantation more

closely resembles epitaxial growth of GaAs than the annealing of damage caused by C implantation. Therefore, we expect C_{As} will form more easily in the highly damaged layers.

Harris[9] found the activation of C (implanted at an energy of 200 keV and dose of 2 x 10^{14} cm^{-2}) increased from 1% to 8% when implants were performed at 77K and created an amorphous layer in the substrate. C implanted alone in InGaAs and AlInAs does not produce any measurable electrical activity; however Ar co-implantation resulted in 11% activation of C implanted at a dose of 5 x 10^{14} cm^{-2} and energy of 60 keV.[12] A plausible conclusion from these preliminary results is that additional damage is required to provide substitutional sites for C within the GaAs lattice.

Heckingbottom and Ambridge[13] proposed that maintaining stoichiometry during implantation and annealing in GaAs would increase the electrical activation of implanted ions. When C is implanted into the lattice and substitutes for an As atom either an As interstitial or a Ga vacancy must be created, affecting the stoichiometry of the substrate. The interstitials and vacancies created will degrade the electrical characteristics of the material either by their own electrical nature or by interacting with other defects, forming complexes or defect clusters. The As interstitials can combine with a Ga vacancy creating an As antisite. In the case of co-implantation, the implanted Ga can annihilate a Ga vacancy and thus preserve the stoichiometry of the crystal.

EXPERIMENTAL

In an attempt to separate the major effects enhancing carbon activation, radiation damage and stoichiometry, the following elements were co-implanted: B, N, Al, P, Ar, Ga, As, Kr. The group III elements: B, Al, and Ga, should help restore the stoichiometry during the implantation and annealing procedures while N, P and As co-implants should lead to even larger deviations from stoichiometry. The inert gases: Ar and Kr, are not expected to affect the stoichiometry of the crystal since they exhibit no preferential bonding configuration. Their location in the lattice will be determined by forces such as elastic fields or the presence of dislocations. The atomic masses of the co-implanted elements ranged from 11 amu (B) to 84 amu (Kr).

The GaAs substrates used for implantation were semi-insulating (100) Czochralski grown wafers from the M/A-Com Advanced Semiconductor Division. Before implantation the substrates were solvent cleaned and etched in concentrated HCl for 1 minute. Singly ionized C was implanted with an energy of 40 keV at a dose of 5 x 10^{14} cm^{-2}, with the wafers tilted a few degrees away from the [100] direction to prevent channeling. The co-implant species were implanted following the C implantation, at a dose and energy chosen so that the profile of the co-implant matched the C profile according to LSS theory.[14] Energy and doses for the co-implants are given in Table I. Substrates were held at room temperature during implantation. Following implantation the samples were annealed in a Heatpulse 210 rapid thermal annealer (RTA) at 800°C for 10 s or 950°C for 10 s in flowing forming gas (90% N_2/10% H_2) using the proximity method.

Table I. Implantation parameters.

Implant	Atomic Mass (amu)	Energy (keV)	Dose (cm^{-2})
C	12.0	40	5 x 10^{14}
B	10.8	30	6 x 10^{14}
N	14.0	40	5 x 10^{14}
Al	27.0	80	6 x 10^{14}
P	31.0	90	6 x 10^{14}
Ar	39.9	115	5 x 10^{14}
Ga	69.7	180	5 x 10^{14}
As	74.9	220	4 x 10^{14}
Kr	83.8	250	4 x 10^{14}

Carrier concentration, mobility and resistivity were determined by van der Pauw geometry Hall effect measurements. The amount of damage due to implantation and the subsequent annealing of the damage was measured using channeling Rutherford backscattering spectrometry. Channeling experiments were performed in the <111> direction using 1.95 MeV He^+ ions.

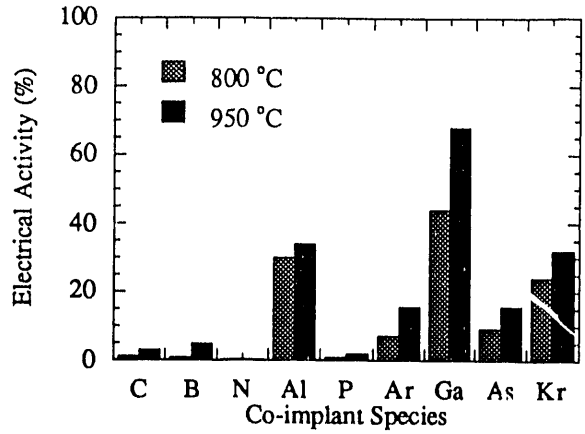

Figure 1. Electrical activity of implanted carbon as a function of co-implant species and annealing temperature. Activity is the ratio of sheet carrier concentration to implant dose.

RESULTS

Figure 1 shows the activation of C as a function of co-implant and annealing temperature. The electrical activation is determined by the ratio of sheet carrier concentration to ion implant dose. Several trends are noticeable. For the co-implant species of column III (B, Al, Ga), activation increases with increasing atomic weight. This trend is also found for the co-implants from column V (N, P, As) and for the two inert gases (Ar, Kr). However for co-implants with similar atomic weights, (i.e., those from the same row of the periodic table) highest activation is found for the group III co-implant followed by the inert gas and then the group V. The lightest co-implants used (B, N) have very little effect on the electrical properties. The effect of both increasing atomic mass and the chemical nature of the co-implant is shown in Figure 2, a plot of sheet hole concentration as a function of atomic mass. Electrical activation and Hall mobilities were higher following annealing at 950°C in all samples except those implanted with C and N.

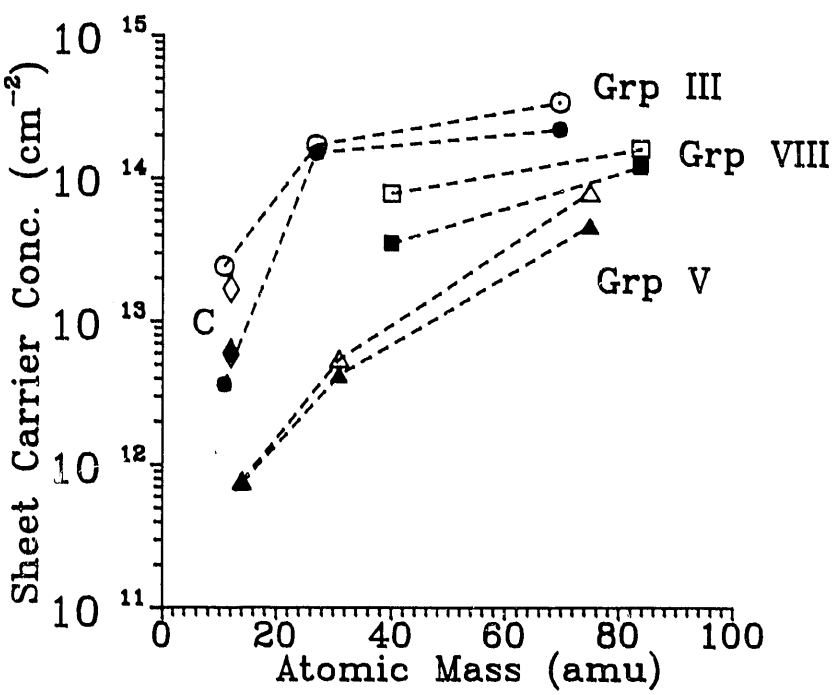

Figure 2. Sheet free hole concentration as a function of atomic mass. Co-implants from columns in the periodic table are plotted separately.
○ Group III 950°C, 10 s
● Group III 800°C, 10 s
□ Group VIII 950°C, 10 s
■ Group VIII 800°C, 10 s
Δ Group V 950°C, 10 s
▲ Group V 800°C, 10 s
◊ Carbon alone 950°C,10s
◆Carbon alone 800°C,10s

The highest free carrier concentration was attained for the case of the C + Ga implant annealed at 950°C for 10 s. The sheet carrier concentration was determined to be 3.4 x 10^{14} cm^{-2}, corresponding to a electrical activation of 68%. To our knowledge, this is the highest electrical activation of C ever reported for such high implant doses.

RBS channeling results are shown in Figure 3 for samples implanted with C+B, C + Al, and C + Ga. Implantation of C + Ga results in an amorphous layer at the surface which is

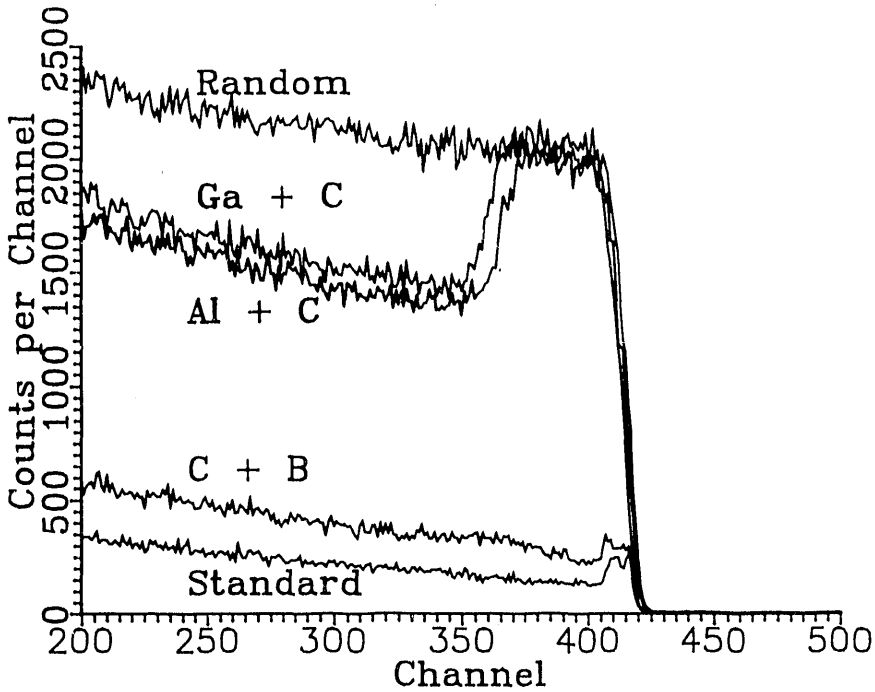

Figure 3. Backscattered particle yields for 1.95 MeV He^+ ions incident upon the <111> channeling direction for layers implanted with C and various group III elements. The amorphous layer at the surface of the C + Ga implanted sample is approximately 140 nm thick. The amorphous layer at the surface of the C + Al implanted sample is approximately 120 nm thick.

approximately 140 nm thick. Similar results (140 nm thick amorphous layers) were attained for C + As and C + Kr implants. C + Al implantation (also C + P and C + Ar) create an amorphous layer which is about 120 nm thick. The B + C, C only and C + N implants do not create an amorphous layer. Some damage in the latter three cases is seen at the end of the range of the ions where the dechanneling rate is slightly higher than that in the standard (unimplanted) sample.

Results from RBS for the C + Ga samples following annealing are shown in Figure 4. The sample has recovered only slightly following the 800°C anneal, but following annealing at 950°C the RBS spectrum is nearly identical to that of the unimplanted sample. Some extended defects remain as seen by the higher dechanneling rate relative to the standard sample. The C + Kr has a higher concentration of residual defects than the C + Ga sample following 950°C annealing as seen in Figure 5.

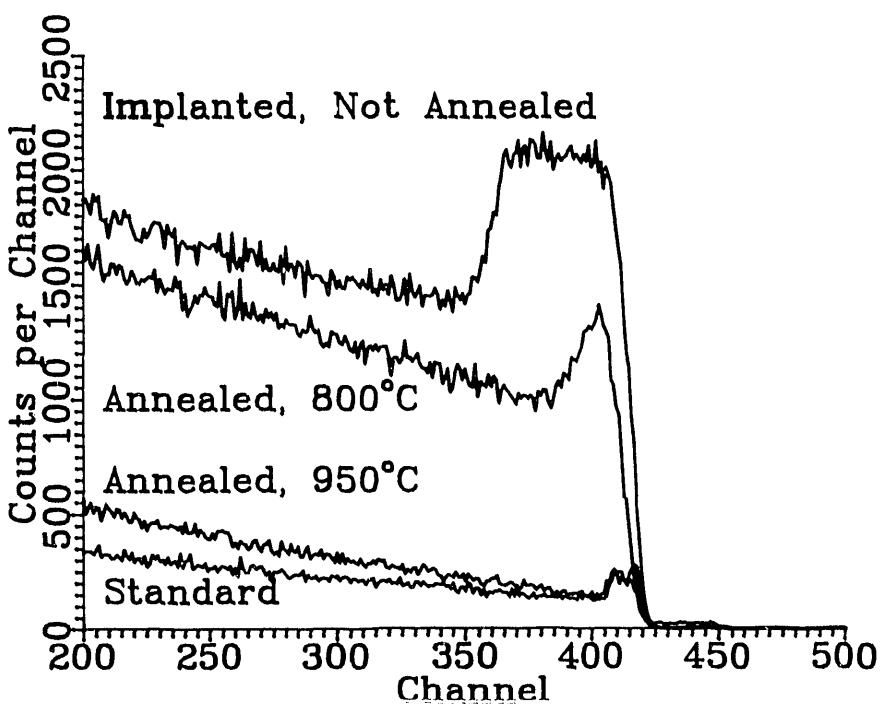

Figure 4. Backscattered particle yields for 1.95 MeV He^+ ions incident upon the <111> channeling direction for layers implanted with C and Ga under various annealing conditions.

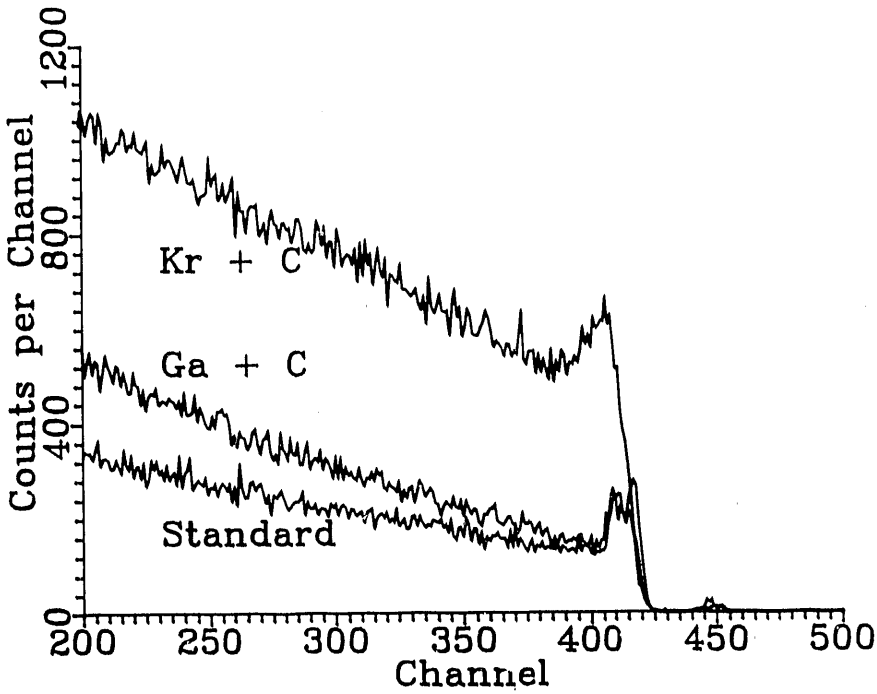

Figure 5. Backscattered particle yields for 1.95 MeV He^+ ions incident upon the <111> channeling direction for layers implanted with C and either Kr or Ga following a 950 °C, 10 sec anneal.

DISCUSSION

Clearly, the increased activation of C following co-implantation with Ga is not due to a stoichiometric effect only. The results presented here show that increasing the amount of damage in the implanted layer increases the free carrier concentration. RBS experiments show that co-implants with atomic weights greater than that of Al create an amorphous layer. This damage plays a significant role as is borne out by the increased activation due to both the Ar and Kr co-implants. Even As, which should affect the stoichiometry in such a way as to hinder C_{As}, increases the activation to some degree.

However, stoichiometry does have an effect on the electrical activity of C. The group III elements result in higher free carrier concentrations compared to other co-implants of similar atomic mass (same row of the periodic table). The N co-implant results in electrical activity less than that of C implanted alone. Ga co-implants provide the best activation (>60% for 950°C anneal, Fig. 2) of any co-implants used in this study.

The C + B implantation provides a key insight into C activation. The co-implantation of B appears to have no effect on the implanted layer. The differences in the electrical properties of the C + B implants and the samples implanted with C alone are statistically insignificant. RBS experiments indicate no additional measurable damage is caused by the co-implant of B. These results suggest that the degree of disorder created in the substrate during implantation determines the electrical activity of the C and that stoichiometry effects alone do not change the activation. B implantation creates no additional damage and therefore does not enhance the electrical activity of the C.

Better electrical characteristics are achieved following annealing at the higher temperature in all samples except those implanted with C + N. As carrier concentration increases the mobility is expected to decrease due to ionized impurity scattering. However, hole concentration and mobility are higher in samples annealed at the 950°C than in samples annealed at 800°C. These results show that annealing at the higher temperature further removes the implantation damage and increases the electrical activation and the mobility. RBS results for samples implanted with C and Ga indicate the extent to which crystallinity is recovered at the two temperatures. Considerable damage remains following annealing at 800°C but after annealing at 950°C the substrate is nearly completely recovered.

Although a similar amount of damage is caused by the Kr and Ga co-implants, more residual defects remain in the C + Kr implanted sample following the 950°C anneal than in the C + Ga implanted sample. The inert gases (Ar and Kr) will not affect the stoichiometry of the crystal, however they do create disorder in the crystal whether they sit substitutionally or

interstitially or form clusters. The effect of these ions is seen in the defects remaining in the substrate following the 950°C anneal as shown by the higher backscattered signal. (Fig. 5)

A systematic study to find the optimum annealing conditions has not been conducted. However it is clear that the 800°C, 10 s annealing process is not sufficient to fully restore the lattice. For the highly damaged case, extended defects remain that require higher temperatures to repair.[15] Pearton and Abernathy[11] attained optimum electrical characteristics following the implantation of Ga and C (Ga was implanted first) after annealing at 800°C for 10 s. However, Shin et. al.[10] achieved the highest activation following a 900°C anneal. The results presented here clearly show temperatures above 800°C are required to fully anneal the damage resulting from implantation of heavy ions such as Ga. A more systematic study of the electrical characteristics and damage recovery as a function of annealing parameters is required to determine the optimum annealing conditions for co-implantation of a heavy ion with C.

CONCLUSIONS

The role of co-implantation in the activation of carbon in GaAs is at least two-fold: stoichiometry and damage have an effect. A certain degree of disorder (possibly an amorphous layer) must be created in the substrate. Once the disorder is created, maintaining stoichiometry during the implantation and annealing process further increases the electrical activity. The highest electrical activity, 68%, was achieved in the C + Ga implants following a 950°C anneal. To our knowledge, this is the highest electrical activation reported.

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