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FORMATION OF HEAVILY DOPED N-TYPE LAYERS IN GaAs BY MULTIPLE ION IMPLANTATION

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N-type layers in GaAs with high free electron concentrations have been produced by multiple implantation of Ga, As, or P with dopant species such as Se, Si, or Ge. The implants that have been investigated include Si, Si + P, Ge, Ge + As, Se, and Se + Ga. The multiple implants Si + P, Ge + As, and Se + Ga gave higher peak carrier concentrations, especially at lower anneal temperatures, than did the respective single implants Si, Ge, and Se. In fact, Ge when implanted alone produced a p-type layer while the Ge + As multiple implant produced an n-type layer. Multiple implants with Si and Ge as dopants showed significant thermal diffusion during the anneal. Multiple implants of Ga with Se, on the other hand, resulted in reduced thermal diffusion in comparison with single Se implants.

Key words: gallium arsenide, ion implantation, sheet resistivity, doping, multiple implantation

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Definitions

Multiple implantation: Sequential implantation of more than one type of ion. Each ion species is implanted in a conventional manner.

Co-implantation: Any method of implantation which results in the introduction of atoms of more than one element into the target material. Includes multiple implantation.

Complementary species: An ion species which, when co-implanted with other ion species in proper proportion, results in minimal changes in the stoichiometry of the target.

Introduction

The doping of compound semiconductors by ion implantation is complicated by the possibility of induced stoichiometric changes. Multiple ion implantation has been introduced as a means for controlling the stoichiometry in the implanted layer.([1,2,3]) Itoh and Kushiro([4,5]) have used As co-implantation with Cd and Te to prevent formation of intrinsic layers beneath the implanted layers. Itoh and Oana([6]) noticed increased p-type activity resulting from phosphorus co-implantation with Zn in $GaAs_{0.62}P_{0.38}$. Co-implantation of Ga, As, and P with Zn into $GaAs_{0.6}P_{0.4}$ and GaAs was shown by Stoneham and Gibbons([2,3]) to strongly affect the degree of zinc diffusion during the anneal.

Multiple implantation has recently been explored as a means of producing heavily doped n-type layers with high carrier concentrations and low sheet resistivities in GaAs. An encouraging result has been reported by Woodcock([7]), who co-implanted Ga with Se to obtain a peak carrier concentration of $5 \times 10^{18} cm^{-3}$, an order of magnitude above that obtained with Se implanted alone and annealed at the same temperature of 750°C. Reported in the present paper are some results of a more comprehensive study of multiple implants involving the dopants Si, Ge, and Se.

Experimental

To reduce the complexity of the study, several of the variables were held fixed. All implants were performed with the GaAs samples initially at room temperature and with their polished surfaces normal to the incident ion beam.* Semi-insulating Cr-doped [100] GaAs substrates were used for the implants involving Si or Ge, and similar substrates covered with lightly doped (10^{14} cm^{-3}) n-type LPE buffer layers 2-4 microns thick were used for all the other implants. Implantation experiments comparing the bare semi-insulating material with the buffered material failed to show any differences significant to this study. Table I lists the implant species used and the energies at which they were implanted in all of the experiments. In every multiple implant, the dopant species (Si, Ge, Se) were implanted first, and the complementary species (P, As, or Ga) were implanted second. The dose of the complementary species was set equal to that of the dopant species in order to minimize the effect of the implant on stoichiometry. The implantation energy of each of the complementary species was chosen, as shown in Table I, to give it approximately the same projected range distribution as that of the corresponding dopant species. For the Si and P implants, one-third of the total dose of each species was implanted at a lower energy than that of the remaining two-thirds in order to produce a flatter depth distribution.

Table I. Implant species and energies.

DOPANT SPECIES	ENERGY	COMPLEMENTARY SPECIES	ENERGY
$^{28}Si^+$	2/3 at 187 keV 1/3 at 75 keV	$^{31}P^+$	2/3 at 200 keV 1/3 at 80 keV
$^{74}Ge^+$	200 keV	$^{75}As^+$	200 keV
$^{80}Se^+$	200 keV	$^{69}Ga^+$	200 keV

*Channelling was not expected to be significant since the ion doses were well above the disorder threshold.

After implantation all samples were capped with 7000Å of CVD SiO_2 deposited at 450°C and were annealed in flowing H_2. Differential van der Pauw measurements were used to obtain the resulting carrier concentration and Hall mobility profiles. The carrier concentrations were computed under the assumption that drift mobility and Hall mobility were equal; hence the actual carrier concentrations may be somewhat higher than those indicated by the graphs.

Results

To determine whether the annealing method used in this study might introduce carriers into the material, unimplanted samples were annealed at temperatures ranging from 850°C to 1050°C. Subsequent analysis with van der Pauw measurements failed to reveal any conducting layers. To determine what direct effects the implantation of complementary species might have on GaAs, samples were implanted with P alone and with Ga alone. After an anneal at 1000°C for 15 minutes, the samples had conducting layers on the surfaces as described in Table II. In both cases the sheet carrier concentrations were very small in comparison with the implant doses.

Table II. P and Ga implants.

SPECIES	DOSE (cm^{-2})	CONDUCTIVITY TYPE	PEAK CARRIER CONC (cm^{-3})	DETECTABLE DEPTH (Å)
$^{31}P^+$	7.5×10^{15}	n	$\sim 10^{17}$	5000
$^{69}Ga^+$	1.0×10^{16}	p	$\sim 10^{18}$	5000

ANNEAL: 1000°C for 15 min.

The van der Pauw profile for a multiple implant of Si + P annealed at 850°C is compared in Figure 1 to the profiles for some implants of Si alone annealed at the same temperature. All of the profiles show about the same depth, but none of the Si implants come close to the Si + P implant in peak carrier concentration or average carrier mobility. Another comparison is shown in Figure 2 for samples annealed at 1050°C.

At this higher anneal temperature an implant of Si alone (providing the dose is not too high) is observed

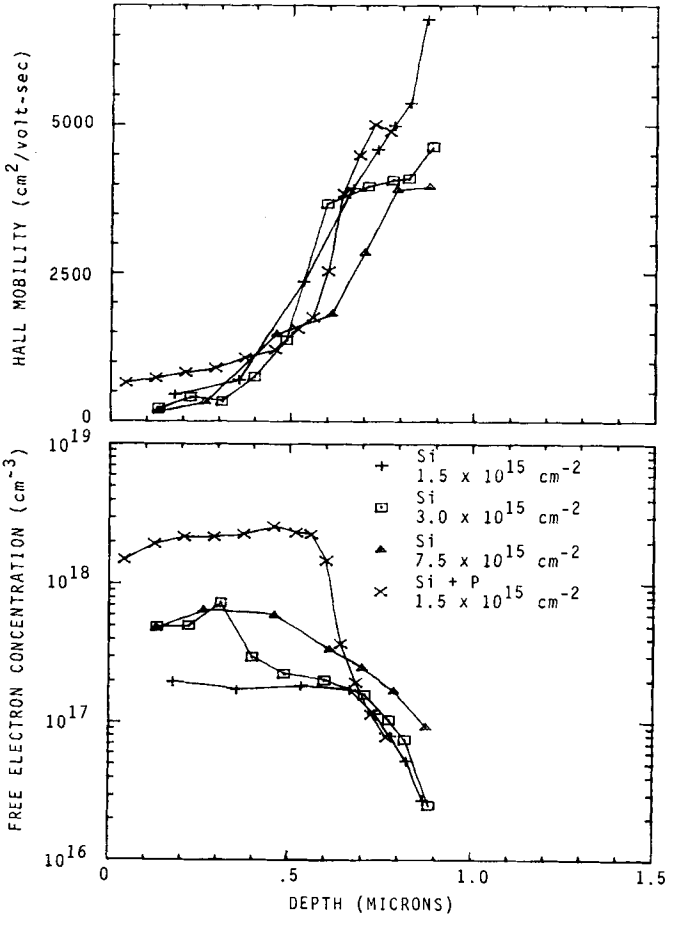

Fig. 1 Van der Pauw profiles for Si and Si + P implants annealed at 850°C for 15 min.

to produce a peak carrier concentration nearly equal to that produced by the Si + P multiple implant. However, the donors in the Si + P implant appear to have diffused considerably while the implants of Si alone show no diffusion beyond the depths observed for the lower anneal temperature of Figure 1.

The effect of anneal temperature on the free electron distribution resulting from a Si + P multiple

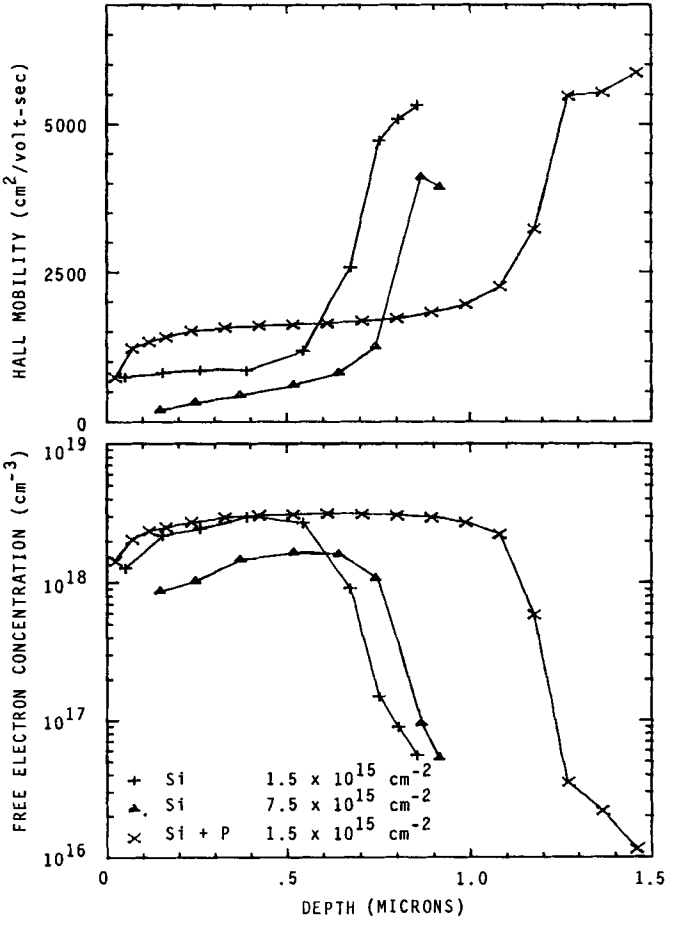

Fig. 2 Van der Pauw profiles for Si and Si + P implants annealed at 1050°C for 15 min.

implant is displayed in Figure 3. The peak carrier concentration changes little with anneal temperature, seemingly having reached a saturation point at about 950°C. Diffusion is once again evident as the profile depth increases with anneal temperature.

Figure 4 shows the effect of dose on the profiles of Si + P implants annealed at 1000°C. A substantial degree of dose-dependent diffusion is evident with the highest

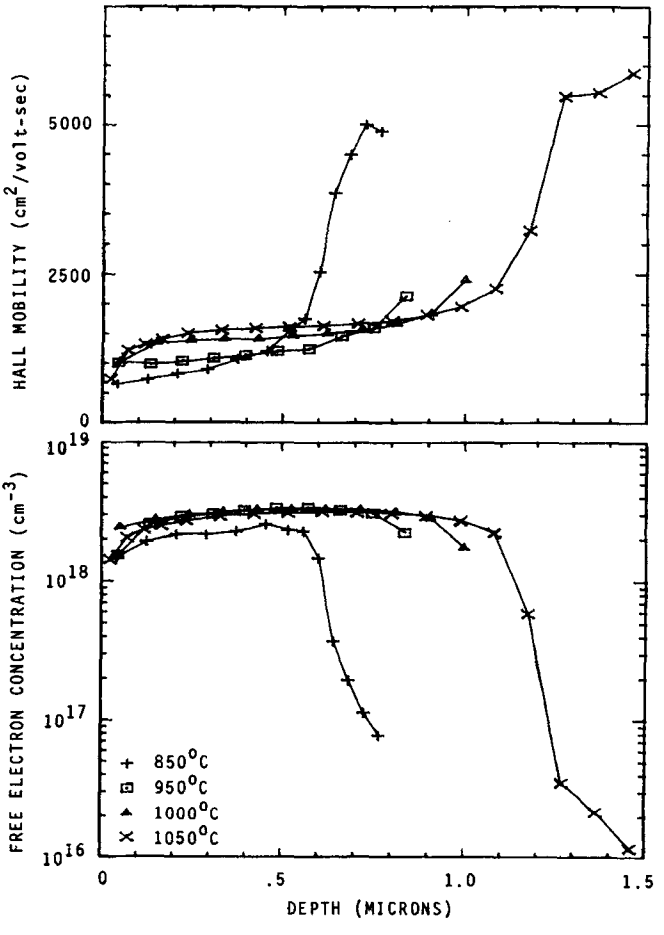

Fig. 3 Van der Pauw profiles for a Si + P implant with a Si dose(=P dose) of 1.5 x 10^{15}cm^{-2} annealed at four different temperatures.

dose giving a depth of 2 microns. Once again the peak carrier concentration appears to have saturated at about 5 x 10^{18}cm^{-3}. The second-deepest profile in Figure 4 showed the lowest sheet resistivity -- less than 9 ohms per square.

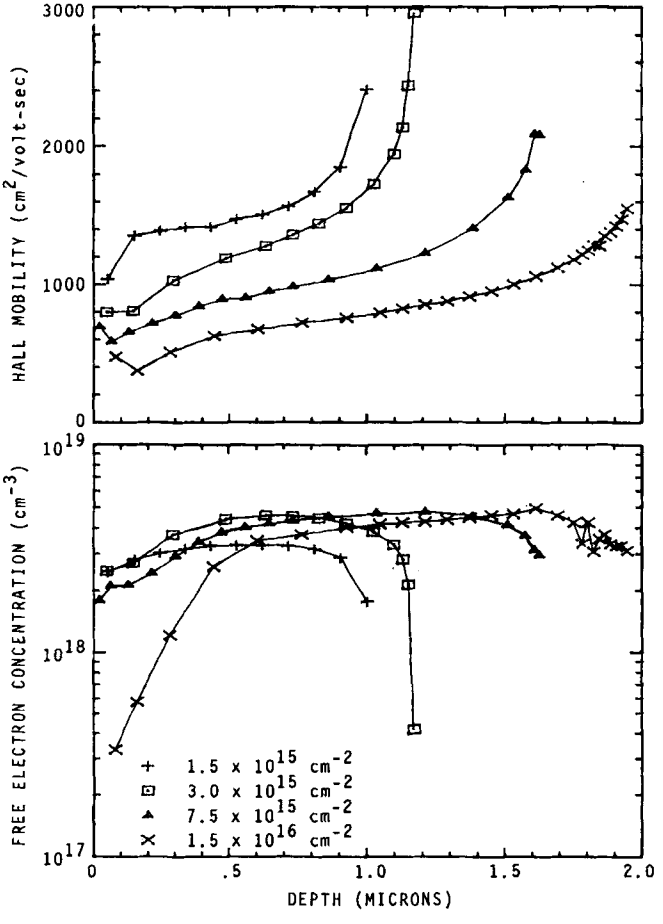

Fig. 4 Van der Pauw profiles for Si + P implants with four different Si doses (=P doses). All four were annealed at 1000°C for 15 min.

Implants involving Ge behaved somewhat differently from those involving Si. Figure 5 shows profiles for multiple implants of Ge + As with three different doses. The peak carrier concentration does not show such a decisive saturation as was observed in Si + P implants, and the highest value reached, $1.8 \times 10^{18} cm^{-3}$, was lower than that reached in Si + P implants.

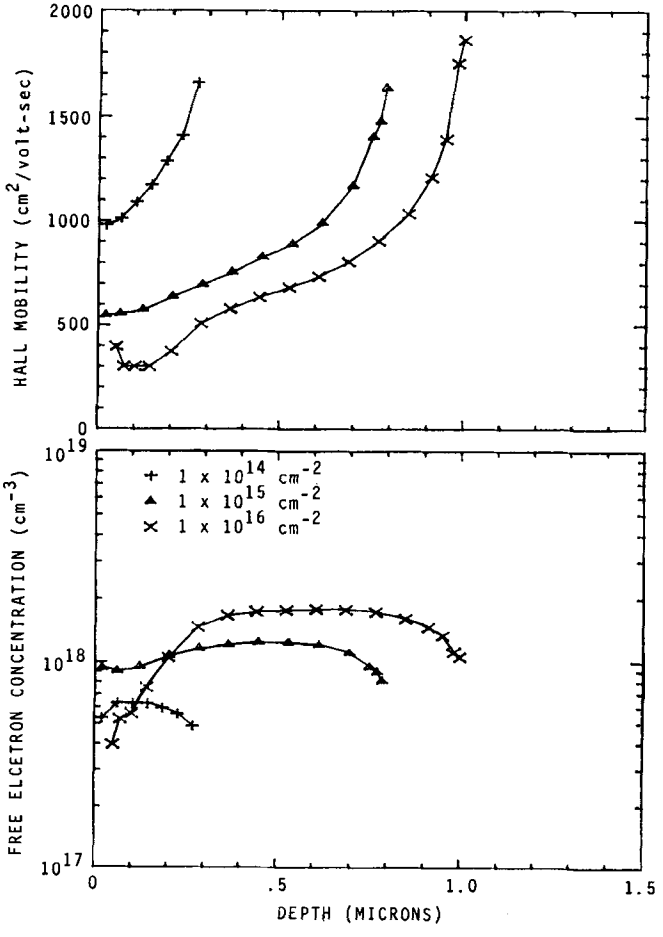

Fig. 5 Van der Pauw profiles for Ge + A_S implants with three different Ge doses (=A_S doses). All three were annealed at 1000°C for 15 min.

Like the Si + P implants, however, the Ge + A_S implants appear to exhibit dose-dependent diffusion. Implants of Ge alone corresponding to the multiple implants in Figure 5 yielded p-type layers for the two higher doses and a highly compensated n-type layer for the $1 \times 10^{14}cm^{-2}$ dose. The largest Ge dose gave a peak hole concentration of about $6 \times 10^{18}cm^{-3}$ and a detectable depth of about 5000Å.

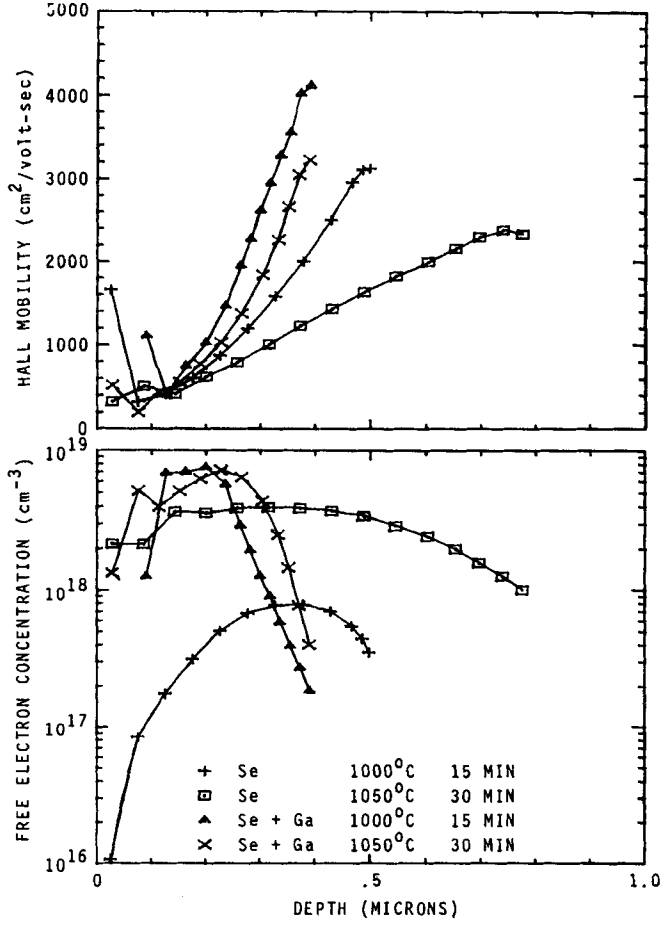

Fig. 6 Van der Pauw profiles for Se and Se + Ga implants. The Se dose in each implant was $1 \times 10^{16} cm^{-2}$.

Single and multiple implants involving Se, a column VI impurity, yielded the profiles shown in Figure 6 for two different anneals. With the milder anneal at 1000°C, the Se + Ga multiple implant shows a peak carrier concentration an order of magnitude higher than that of the corresponding implant of Se alone. For the stronger anneal at 1050°C, the Se + Ga profile shows little difference from that obtained with the milder anneal except for some diffusion-like spreading. The

profiles for the implants of Se alone, however, show a higher peak carrier concentration and a significantly greater depth under the stronger anneal than under the milder anneal. In general, multiple implantation of Ga with Se leads to shallower profiles and higher peak carrier concentrations, the highest obtained being $7.6 \times 10^{18} cm^{-3}$.

Discussion

A general trend is evident throughout this study: for each of the dopant species investigated, the additional implantation of an equal dose of a complementary species leads to higher peak free electron concentrations, especially at the lower anneal temperatures, than those obtained without multiple implantation.

This trend supports the contention that preservation of stoichiometric balance in high-dose implants helps to assure activation of the dopant and to reduce compensation by native defects or complexes. A reduction in the concentration of native defects and complexes in the implanted layer is also indicated by the higher mobilities (see Figures 1, 2 and 6) for the multiple implants compared to those of the corresponding implants of dopant ions alone. The fact that multiple implantation makes less of an improvement in peak carrier concentration for Si and Se dopants when higher annealing temperatures are used can reasonably be attributed to the diffusion of defects resulting from nonstoichiometry. Given a high enough annealing temperature and a long enough time, one can expect the native defects produced by a nonstoichiometric implant to diffuse away from the implanted layer. Hence, the practical effect of using multiple implantation to maintain stoichiometric balance is to reduce the annealing temperature and time required to achieve a given degree of activation.

The fact that the profiles obtained for Se + Ga multiple implants were significantly shallower than those obtained for corresponding implants of Se alone (see Figure 6) suggests that Ga co-implantation inhibits Se diffusion. Support is thus added to A. Lidow's theory ([8]) that active Se diffuses very slowly in GaAs while a neutral selenium-gallium vacancy complex (Se-V_{Ga}) diffuses

more rapidly. Gallium co-implantation can be expected to reduce the concentration of gallium vacancies available for forming the Se-V_{Ga} complex and should therefore slow the rate at which Se diffuses.

The unusual diffusion effects displayed by Si + P multiple implants (Figures 2, 3 and 4) are not so easy to explain. One possibility is that it is normal for Si at high concentrations to diffuse rapidly and that the defects associated with the stoichiometric imbalance produced by an implant of Si alone tend to trap the Si and inhibit its diffusion. Another possibility is that Si diffuses rapidly only when the gallium vacancy concentration is high enough (due to P co-implantation) to form rapidly diffusing Si-V_{Ga} complexes. The understanding of these phenomena require further study.

Summary

High-dose multiple implants of Si + P, Ge + As, and Se + Ga have been investigated and compared to the respective single implants of Si, Ge, and Se in GaAs. In general, the multiple implants yielded higher peak carrier concentrations, especially at lower anneal temperatures, than did the single implants. Multiple implants involving Si and Ge displayed pronounced dose-dependent diffusion, with the depth increasing with dose and with anneal temperature. Co-implantation of Ga with Se significantly inhibited diffusion of the Se. The lowest sheet resistivity obtained for n-type implanted layers in this study was less than 9 ohms per square, and the highest free electron concentration obtained was $7.6 \times 10^{18} cm^{-3}$ as measured by the differential van der Pauw technique.

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