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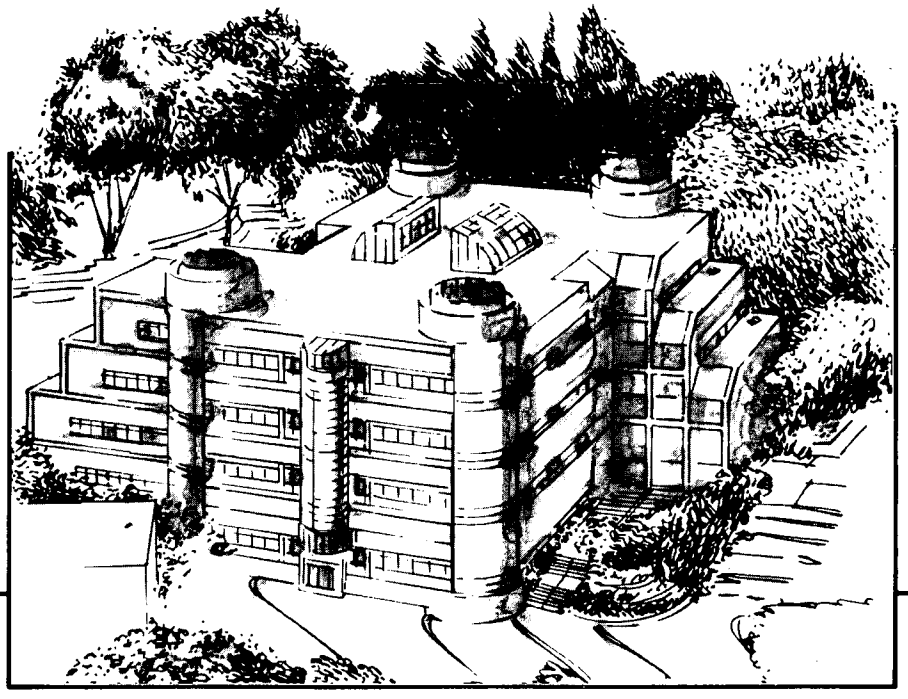

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Key words: Implantation, GaAs, Native defects, compensation

ABSTRACT

The effects of co-implantation on the electrical activity of C acceptors have been studied using a series of elements as co-implants. A variety of electrical and structural techniques were used for characterization. It is found that although co-implantation with heavy ions improves the substitutionality of C atoms on As sites, a high electrical activity of the C_{As} acceptors is attained only if the stoichiometry is maintained through co-implantation of group III atoms.

I. INTRODUCTION

Ion implantation has evolved into the standard doping technology in the semiconductor industry. Its principal advantages are the control of the doping profile and the large variety of dopant species. In elemental semiconductors such as Ge and Si, activation of implanted dopants is a relatively straightforward process. In general, once the implanted ion occupies a substitutional site, it is an electrically active dopant. However, in compound semiconductors the activation of implanted dopants is more complicated..

In a compound semiconductor, the implanted ions are expected to occupy one sublattice exclusively. Consider C implanted into GaAs. C is a group IV element and occupies an As site, acting as an acceptor. Native defects associated with the non-stoichiometry due to the excess of As or deficiency of Ga are present in the implanted layer. These native defects can compensate the implanted dopants or passivate the dopants by forming complexes with the implanted ions. In both cases, the number of free carriers is reduced, resulting in less than 100% activation of implanted C ions.

Co-implantation of a complementary species to maintain the stoichiometry of an implanted layer in compound semiconductors was originally suggested by Heckingbottom and Ambridge.[1] In the case of C implanted into GaAs, Ga is co-implanted with an energy and dose chosen to match the profile of the implanted C ions. The stoichiometry of the implanted layer is then maintained during the implantation and annealing processes resulting in fewer native defects which can compensate or passivate the C acceptors.

C is an excellent p-type dopant in GaAs. Its diffusion coefficient is significantly lower[2] than that of group II p-type dopants such as Mg and Zn.[3, 4] Ultra-high doping levels ($p>10^{20}$ cm^{-3}) have been attained with epitaxial growth.[5, 6] However, implantation of C is not as successful. Implanted alone, activation of C is less than 10%.[7, 8] With a Ga co-implant, activation can increase significantly,[9] as high as 65%.[10].

The mechanism by which the Ga co-implant increases the activation of C is unclear. Although the Ga co-implant maintains the stoichiometry of the implanted layer, it also increases the amount of radiation damage to the substrate. C has an atomic mass of 12 and when implanted

into GaAs causes little lattice damage. The concentration of defects is further reduced by self-annealing during the room temperature implantation process. The Ga co-implant causes considerably more damage to the substrate, increasing the number of As vacancies available for the implanted C ions. Co-implantation with heavy inert atoms (Ar and Kr) has been shown to increase the activation of Si in GaAs [11] and C in GaAs.[12] Therefore both increasing the radiation damage and maintaining the stoichiometry of the substrate increase the activation of implanted C in GaAs.

In this paper, we report on our studies of the effects of stoichiometry and damage and the role of native defects on C activation in GaAs. A series of different co-implant ions were used: B, N, Al, P, Ar, Ga, As, and Kr. The group III elements (B, Al, and Ga) help to maintain the stoichiometry of the implanted region. The noble gasses (Ar and Kr) should not affect the stoichiometry while the group V elements (N, P, and As) create even larger deviations in stoichiometry than implantation of C alone. As the atomic mass of the co-implant species increases, the radiation damage density in the substrate due to the implantation process increases. This increase is due to the larger mass of the implanted ion and the higher implantation energy required to match the C ion implantation profile.

II. EXPERIMENTAL

Semi-insulating (100) LEC GaAs substrates were solvent cleaned, etched in 12M HCl for 1 minute, and rinsed in de-ionized water before implantation. Singly ionized C ions were implanted into all of the substrates simultaneously at an energy of 40 keV and a dose of 5×10^{14} cm^{-2}. Following implantation of C, the co-implant was performed for individual samples. The dose and energy of the co-implant were chosen to match the profile of the C ions as calculated by the LSS theory.[13] The wafers were tilted 7° off the [100] axis during both implantations to prevent channeling. The substrates were held at room temperature during implantation. Following implantation, the samples were annealed in flowing forming gas (90% N_2 / 10% H_2) at 950 °C for 10 seconds using a proximity cap.

Alloyed contacts of In:Zn were formed at 250°C on 8×8 mm^2 pieces of each sample. Carrier concentration, mobility, and resistivity as a function of temperature were determined by van der Pauw geometry Hall effect measurements. The activation (or electrical activity) is then determined by dividing the sheet free carrier concentration (holes) by the implanted dose.

The amount of structural damage caused by the implantation was characterized by channeling Rutherford backscattering spectrometry (RBS) using 1.95 MeV He^+ ions aligned along the <111> or <110> direction. Photoluminescence measurements of optically active deep levels were made at 4 K using the 488 nm line of an Ar laser.

The relative concentrations of C_{As} were determined with local vibrational mode (LVM) Raman spectroscopy. The LVM of C_{As} has been observed previously by Raman spectroscopy at 583 cm^{-1} at 77 K.[14] Raman spectra were collected with 2 cm^{-1} resolution at room temperature in the $z(x,y)\bar{z}$ pseudo-backscattering geometry. The 488 nm (2.54 eV) line of an Ar ion laser was used. The laser power was 250 mW and typical integration times were 1 hour. The intensity of the C_{As} LVM peak observed at 580 cm^{-1} below the Ar ion laser line was internally calibrated by ratioing the peak height to that of the 2nd-order phonon observed at 525 cm^{-1}.

III. RESULTS AND DISCUSSION

In figure 1, the sheet free hole concentration is plotted as a function of the depth of the amorphous layer due to implantation. The depth of the amorphous layer is determined by channeling RBS. As the radiation damage in the implanted layer increases, the activation of the

implanted carbon increases. In addition, the chemical nature of the co-implant species has an effect. The highest activation levels are attained for the co-implants which are group III elements, followed by the group VIII elements. The lowest activation levels are obtained for the group V co-implants.

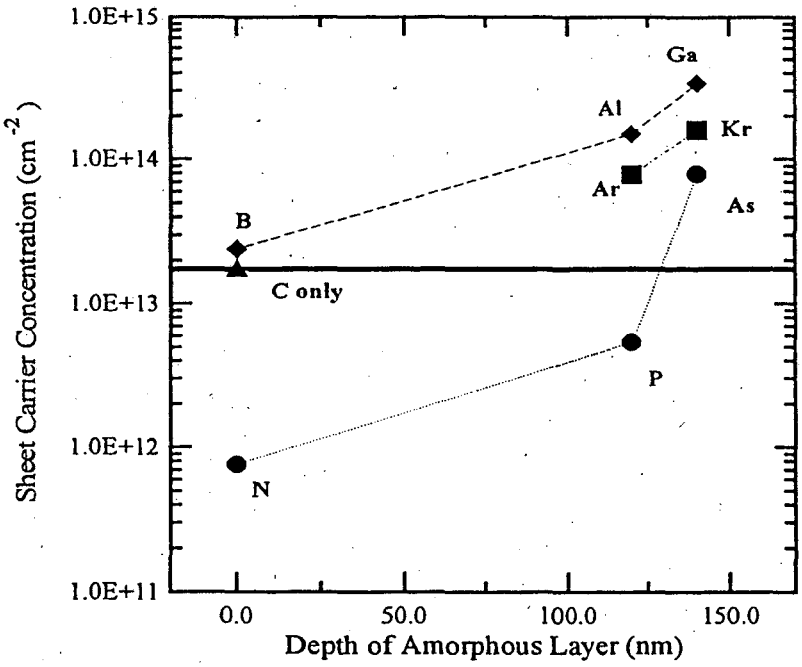

Figure 1. The sheet free hole concentration as measured by Hall effect is plotted as a function of the depth of the amorphous layer due to implantation as measured by RBS.

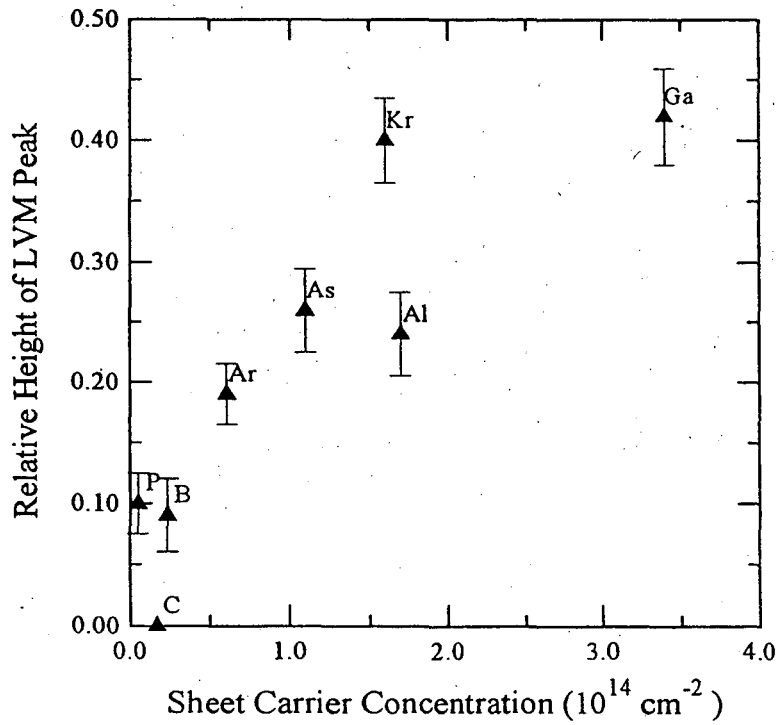

Figure 2. The relative height of C_{As} LVM peak as measured by Raman spectroscopy as a function of the sheet carrier concentration.

The height of the C_{As} local vibrational mode peak as measured by Raman spectroscopy is plotted as a function of the sheet carrier concentration in figure 2. The sheet carrier concentration is not proportional to the concentration of C_{As}. Comparing group III co-implants with group VIII co-implants and considering the RBS results, samples with similar amounts of radiation damage result in similar concentrations of C_{As}. However for co-implants of Al and Ga, the carrier concentration is significantly higher than for samples co-implanted with Ar and Kr, respectively.

Our low temperature Hall effect and photoluminescence measurements suggest that in the samples co-implanted with Ar or Kr, a portion of the C_{As} acceptors are compensated. As shown in figure 3, the C+Kr sample has lower Hall mobilities at all temperatures than the C+Al sample. Since the two samples have the same number of free carriers, the lower mobility indicates greater ionized impurity scattering due to compensating defects. The photoluminescence results shown in figure 4 further corroborate the existence of compensating defects. The deep defect related photoluminescence is more intense in the C+Kr and C+Ar (not shown) samples than in the C+Al and C+Ga (not shown)

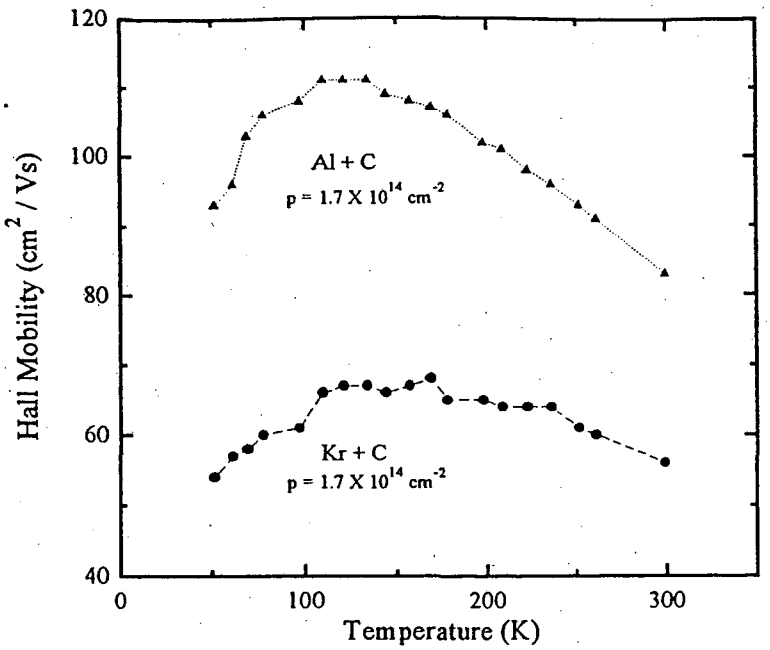

Figure 3. The Hall mobility of the free holes as a function of temperature for the Al+C and Kr+C samples.

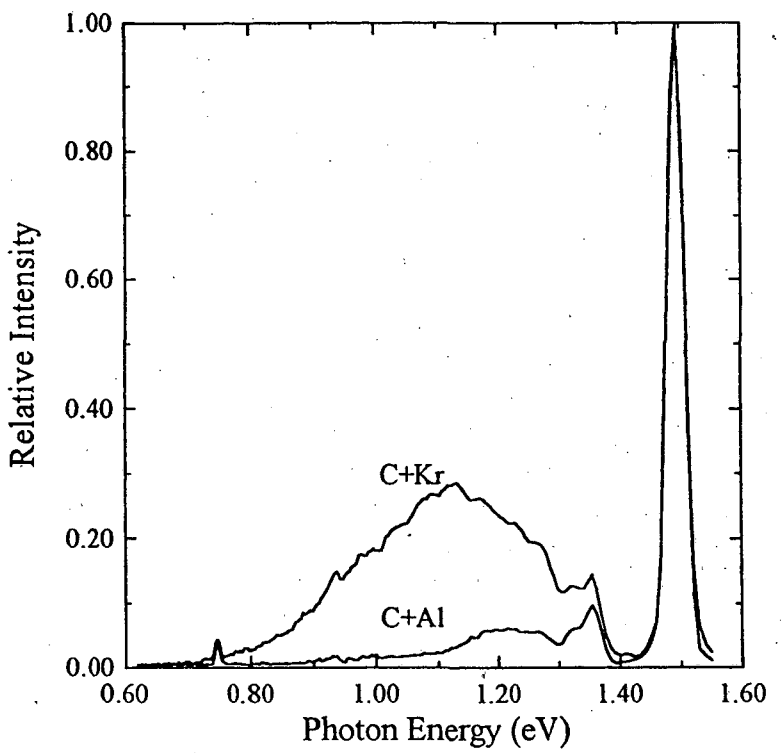

Figure 4. Relative intensity of photoluminescence as a function of photon energy for the C+Kr and C+Al samples.

samples. In the C+Ar and C+Kr samples, the deviation from stoichiometry, i.e., the excess As atoms from the sites substituted by C, is accommodated by point or extended defects. As proposed by Walukiewicz[15] in p-type GaAs the defects related to the non-stoichiometry are predominantly donors. Such donor defects can act as compensating centers reducing the free hole concentration.

The group V co-implants (As and P) lead to lower free hole concentrations than the group III and group VIII co-implants of similar atomic mass. In addition, the LVM peaks are smaller indicating the concentration of C_{As} is also reduced. This reduction results from the competition of the As and P co-implants with the C for As vacancies. As and P also introduce additional non-stoichiometry into the crystal increasing the concentration of native defects and further reducing the number of free carriers.

Of particular interest is the sample co-implanted with B. The B co-implant causes little additional radiation damage in the substrate but should help maintain the stoichiometry in the implanted layer. However the free carrier concentration is nearly the same as in the sample implanted with C only. This result indicates that additional radiation damage is required to increase the activation of implanted C.

V. CONCLUSIONS

Co-implantation increases the activation of implanted C in GaAs by two mechanisms: increasing the radiation damage in the substrate and maintaining the stoichiometry in the implanted layer. The additional radiation damage due to the heavy co-implant species provides vacant As sites for the implanted C. Co-implants which cause similar amounts of damage to the substrate, i.e., co-implants with similar atomic weights, have similar concentrations of C_{As}. However this condition is not sufficient to obtain high concentrations of free holes. The native defects resulting from the implantation process compensate the C_{As} acceptors except in the case of group III co-implants which help maintain the stoichiometry of the crystal. The highest activation attained is 65% for the case in which Ga is used as the co-implant.

V. ACKNOWLEDGMENTS

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