Silicon Heavily Doped MBE Grown Al$_{0.3}$Ga$_{0.7}$As Samples

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Silicon heavily doped MBE-grown Al$_{0.3}$Ga$_{0.7}$As samples have been investigated in some detail on their electrical properties considering the presence of a multiplicity of defects and it is shown that their relative concentrations depend on the aluminum content. A maximum free-electron concentration around 4×10^{18} cm^{-3}, far below the maximum for GaAs, has been obtained showing that the aluminum atoms are a hindrance for the incorporation of silicon atoms in the group III element sublattice. The free-electron concentration is rather strongly dependent on the temperature and illumination conditions. The DX center is used to explain this strong dependence. In the absence of DX center the relative concentrations of the multiplicity of simple and complex defects have been studied also as a function of tlie silicon nominal concentration and it has been shown that competition phenomena are present. Equations relating clefect concentrations to experimental parameters are presented.

I. Introduction

Silicon is commonly used as an n-type dopiiig element in AlGaAs alloys grown by molecular beam epitaxy (MBE).

Tlie GaAs:Si bulk layers have been intensively investigated over a very wide range of doping concentra.-tions. Nominally undoped GaAs layers grown by MBE *using elemen;al sources* are generally founcl to be p-type with a liole concentration ranging from 5×10^{14} to 1×10^{15} cm^{-3}. The main residual p-type impurity in MBE grown samples is carbon, which is identified using photoluminescence spectra. It shows the presente of a.shallow acceptor with energy of 26meV at low teinperatures (4.2K).

Intentional incorporation of silicon as doping element for MBE grown GaAs has at first the so-called one to one correspondence regime in which every doping atom produces only a specific kincl of defect, i.e., tlie shallow donors. In this regime the free-carrier concentration n is directly proportioiial to the silicon flux and to the incorporated silicon concentration, indicating that its sticking coefficient is unity and that basically all silicon atom incorporate as donors in the gallium site. The free-carrier concentration increases linearly up to about 7×10^{18} cm^{-3} [1]. At this maximum value the behavior of n changes abruptly, and it starts to fall with further increase in the incorporated silicon concentration. This indicates that a solubility limit is achieved and the reduction indicates that compensation mechanisms operates. Beyond this maximum we have the heavily doped regime when it is expected that the silicon atoms are incorporated in different crystallographic sites originating a multiplicity of defects. Some of them are electrically charged while others are not, which makes it quite difficult to predict and control the properties of the material.

The best known and studied simple defects are produced when silicon atoms incorporate on gallium sublattice sites (Si_{Ga}) as donors or on arsenic sublattice sites (Si_{As}) as acceptors. For alloy samples in the AlGaAs system having an aluminum content higher than about 22% another defect, the so-called DX-center, must also be considered. The best known complex defects[2,3] are produced when silicon atoms incorporate on one of the gallium or arsenic sublattices and are

bound to an intrinsic defect. $(Si_{Ga} - X)$ and $(Si_{As} - Y)$ respectively or when two silicon atoms are incorporated on both gallium and arsenic nearest neighbor sublattice sites $(Si_{Ga} - Si_{As})$. The intrinsic defects X and Y were respectively assigned to gallium and arsenic vacancies. Our samples are within standard MBE growth parameters and the formation of Y was not induced by annealing as seen by PL measurements[3], thus the presence of $(Si_{AS} - Y)$ defect. can be neglected in the present work.

Using local vibrational modes [LVM] spectroscopy, Maguire et al[2] have concluded that in heavily doped GaAs samples with silicon concentration of 3 x 10^{19} cm^{-3} the donors are predominantly compensated by $(Si_{Ga} - X)$ and (Si_{As}).

For some device applications it is desirable to produce heavily doped AlGaAs alloys without significantly degrading the electrical properties. To the best of our knowledge there has been no attempt to determine whether the solubility limit of silicon atoms as donors on the group III element depends on the aluminum content. There is also no systematic study for silicon doping concentration beyond this solubility limit where the other defects are expected to be present. This is probably associated with the presence of the deep level defect, the DX-center, what makes the alloy studies more complicated than for GaAs. It is generally accepted[4] that the presence of the DX center ill silicon doped AlGaAs alloys with an energy level below the conduction band minimum $(x \geq 0.22)$ produces the persistent photocondutivity (PPC) effect, at temperatures below $\cong$ 100K. Persistent photocondutivity is characterized by the increase of the free-carrier concentration after illumination, which has a nonexponential relaxation behavior after the illumination is turned off (typical recombination times range from minutes to days). It is now well accepted[5] that the DX center lias a negative charge resulting from the "reaction" $2d^0 \rightarrow d^+ DX^-$ where d^0 and d^+ are respectively the neutral and ionized hidrogenic-like shallow donor centers. Therefore

the presence of DX center adds a new compensation mechanism for the free-carrier concentration. It should be noted that on heavily doped samples actually all the shallow states are expected to be ionized.

We intend to show how the presence of the multiplicity of defects can be handled when studied on heavily silicon doped MRE grown $Al_{0.3}Ga_{0.7}As$ samples. Our approach consists in investigating the free-carrier concentration and mobility obtained by photo-Hall measurements. We show experimentally for the first time that the maximum free-electron concentration and the relative defect concentrations depend on the aluminum content and we succeeded in evaluating some of the defect concentrations. Based on the influence of the various defects over the electrical properties we have shown also that their concentrations change differently with the silicon nominal concentration. Further studies, especially based on the optical behavior as well as on time-resolved plioto-Hall are being pursued.

II. Experimental

We studied four samples differing only on the silicon nominal concentration in the range of 3×10^{18} cm^{-3} to 3 x 10^{19} cm^{-3} which was based on machine calibration growth parameters. The samples were grown on semi-insulating Cr-doped GaAs(OOl) substrates. A (0.3 μm thick) non- intentionally doped GaAs buffer layer was followed by a.non-intentionally doped $Al_{0.3}Ga_{0.7}As$ (0.5 μm thick). The active layer (2.5 μm thick) a heavily silicon doped $Al_{0.3}Ga_{0.7}As$ was then grown. The structure was finished with a silicon doped GaAs cap layer with a.thickness of approximately 60Å. The substrate temperature was 620°C. The sample #1 was grown under the supposition that all silicon atoms would be incorporated as shallow donors or then as DX-center. Hall measurements were carried out on a. photolitographically fabricated bridge, and to illuminate the sample we used an infrared ($h\nu = 1.32eV$) light emitting diode (LED), mounted in the cryostat. We have measured the free-carrier concentration and mobility with the sample

a.t a temperature of 300K in the clarli and under illumination. Then, the samples were slowly cooled down to 77K (minutes to hours) in darkness, and the measurements repeated in tlie dark, under intense illumination, and after tlie illumination was turned off. Under illumination we tried to ensure the DX saturation condition, which me assumed as tlie point where only a negligible increase (less than 10%) ill tlie free-carrier concentration would be expected for furtlier increase in the LED intensity.

III. Results and discussioii

Tlie Hall electron concentrations and mobilities are listed in table 1 and shown in figure 1. Both the free-carrier concentrations and mobilities a.t 300K are the same in darkness and under illumination, and are listed in tlie table 1 as $n(300K)$ and $\mu(300K)$, respectively. The results at 77K in darkness do not depend on the sample coo down time in the range used (minutes to hours). A; 77K tlie results are the same under illumination and after the illumination was turned off ($n(77K,\text{light})$ and $\mu(77K, \text{light})$ in table 1). This inclicates tha; we were at the DX saturation condition and that indeed no other defects were contributing to the free-carrier concentration. The thick line in figure 1 at the left side of the point of the sample #1 represents the one to one correspondence regime. Tlie three full straight-lines with negative slopes were obtained by linear regression using tlie data for samples #2, 3 and 4 where the compensation mechanisms were present. This linear approximation seems to be good because we did not go far away from the maximum value in the experimental curve. The right part of the thick line was chosen to be the same as the highest of the three straight lines but only on the riglit side of tlie sample #2. The left and tlie right parts of the heavy curve were connected arbitrarily. Similar connections have been done for the other two straight lines with points of tlie samp c #1.

The important characteristic of the thick line is that
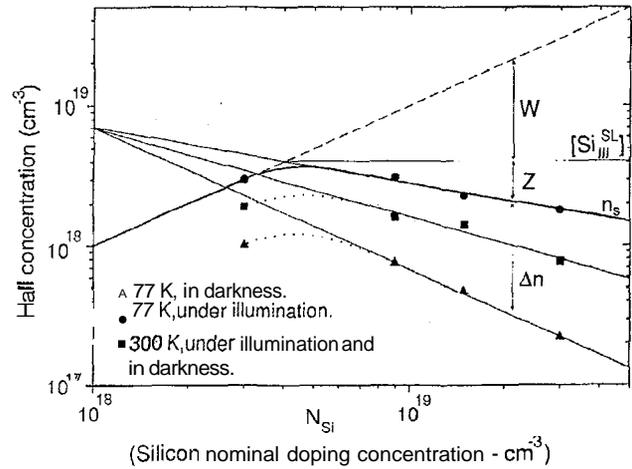
Figure 1: Hall electron concentrations as a function of the intended free-electron concentrations (i.e. the silicon concentrations estimated from tlie doping conditions). The three fiill straight lines were obtained using linear regression leaving out the data of sample #1. The broad line, tlie dashed and tlie two doted lines and the symbols are discussed in the text.

it describes the limit condition when the compensation mechanism associated with the DX center is not present and will hereafter be denoted n_s. Therefore, its maximum value provides the solubility limit of silicon in the site of the group III elements of $Al_{0.3}Ga_{0.7}As$, hereafter denoted $[Si_{III}^{SL}]$, whose value is around 4×10^{18} cm^{-3}. The brackets stancl for concentration. This concentration value is far below the 7×10^{18} cm^{-3} observed for GaAs[1]. This reduction is a strong evidence that compensation mechanisms depend on the aluminum content as suggested previously[6], and that the aluminum atoms are a handicap for the iicorporation of silicon atoms a.s donors in the group III element sublattice. The fact that the bond strength of Al-As is higher than Ga-As may account for the reduction in solubility limit. Indeed, assuming that for small aluminum content the incorporation of aluminum atom prevents completely its site from being occupiecl by a silicon atom, the reduction in the solubility limit of silicon atom on the group III element sublattice is expected to decrease according to the product $(1 - x).[Si_{Ga}^{SL}]$, where x stands for tlie aluminum content and $[Si_{Ga}^{SL}]$ is the solubility limit of silicon atoins for the gallium sublattice in GaAs. In this approximation one obtains $0.7 \times 7 \times 10^{18}$

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Table 1. Data for MBE grown heavily silicon doped $Al_{0.3}Ga_{0.7}As$ samples. All concentrations are in units of cm^{-3}. All mobilities are in units of $cm^2/s.V$.

Samples	1	2	3	4
nominal silicon concentration	3×10^{18}	9×10^{18}	1.5×10^{19}	3×10^{19}
n (77 K, dark)	$(1.0 + 0.1) \times 10^{18}$	$(7.5 + 0.4) \times 10^{17}$	$(4.7 \pm 0.5) \times 10^{17}$	$(2.2 \pm 0.4) \times 10^{17}$
n (77 K, light)	$(3.0 + 0.3) \times 10^{18}$	$(3.1 \pm 0.1) \times 10^{18}$	$(2.3 \pm 0.3) \times 10^{18}$	$(1.8 \pm 0.2) \times 10^{18}$
n (300 K)	$(1.9 \pm 0.1) \times 10^{18}$	$(1.6 \pm 0.6) \times 10^{18}$	$(1.4 \pm 0.2) \times 10^{18}$	$(7.7 \pm 0.1) \times 10^{17}$
μ (77 K, dark)	640	370	320	220
μ (77 K, light)	770	450	510	350
μ (300 K)	740	440	470	350

$cm^{-3} = 4.9 \times 10^{18}$ cm^{-3} as the solubility limit of silicon on the $Al_{0.3}Ga_{0.7}$ sublattice. There is a good agreement between this and the observed value, especially if we coiisider tliat the silicon incorporation in the group III elment could be somewhat increased by optimising growth parameters. Also the slope of the right part of the heavy curve could be somewhat increased negatively due to small deviations from the ideal saturation condition. This last condition is related to the fact that the difficulty to saturate the samples increases with n.

Tliree independent equations will be used to describe our experimental results namely: the free- carrier concentration (eyuation 1), the light induced conversion eyuation between (Si_{Ga}) and DX center (equation 4) and finally tlie total silicon atoms conservation (equation 5). Tlie free-carrier concentration equation is given by

$$n = [Si_{III}] - 2[Si_{III} - X] - [Si_{As}] - [DX] \qquad (I)$$

$[Si_{III}]$ stands for silicon atom concentration yielding shallow donors, the coefficient -2, as suggested by simple chemical considerations, accounts for the state of charge of the complex defect $(Si_{III}-X)$, while the more accepted state of cliarge of the single defects (Si_{rrI}),

(Si_{As}) and DX center is ± 1.

There is now strong evidence[5] that DX center arises from a substitutional donor by itself. Therefore to create one DX center one (Si_{III}) must be destroyed and vice-versa. Tliis lias led to suggestions that DX iiivolves a. displaced doiior with lattice relaxations[7,8]. Earlier supposition that DX should be a complex defect found no experimental support and we will rule out this possibility. There is also no evidence in the literature for a relation between the DX center and the acceptor silicoii in arsenic site. Then we conclude that $[DX]$, $[Si_{III}]$ and free-carrier concentration n are the interdependent terms in equation 1 so that we can define the [DX] independent terms by Z, which will be given by

$$Z \equiv 2[Si_{III} - X] + [Si_{As}] \qquad (2a)$$

$$Z = [Si_{III}] - [DX] - n \qquad (2b)$$

For the saturation condition corresponding to the heavy curve in figure 1 and considering only the right side of the solubility limit one obtains the limit case

$$Z = [Si_{III}^{SL}] - n_s \qquad (3)$$

The light conversion equation, which means that to create one DX center one (Si_{III}) must be destroyed and

vice-versa i:; given for heavily silicon doped samples by

$$[Si^{SL}_{III}] = [Si_{III}] + [DX] \qquad (4)$$

The total silicon concentration is given by

$$N_{Si} = [Si_{III}] + [DX] + [Si_{III} - X] + [Si_{As}] + 2[Si_{III} - Si_{As}] \qquad (5)$$

By separating the DX independent terms in equation 5 we can define W by

$$W \equiv [Si_{III} - X] + [Si_{As}] + 2[Si_{III} - Si_{As}] \qquad (6a)$$

$$W = N_{Si} - [Si_{III}] - [DX] \qquad (6b)$$

$$W = N_{Si} - [Si^{SL}_{III}] \qquad (6c)$$

Using the equations 1, 4 and 5 another one can be deduced, namely the double ionization equation between d^+ and DX^- given by Δn **r** $n_s - n = 2[DX]$.

Therefore, one can see from equations 2a and 6a that if one of three concentrations $[Si_{III} - Si_{As}]$, $[Si_{III} - X]$ and $[Si_{As}]$ is zero or it is determined from a different technique, the other two concentrations can be calculated from Z and W obtained from the experiments we described here. The number of unknown parameters can be even higher than three if other defects are taken into account as for example $(Si_{As} - Y)$. However for our experimental conditions only the three mentioned parameters seem to be the relevant ones.

In order to obtain Z and W only three experimental parameters $[Si^{SL}_{III}]$, N_{Si} and n_s (equations 3 and 6c) are necessary. One of them, namely N_{Si} is a machine calibrated parameter and therefore is not a critical one to be obtained precisely. By using high light intensity practically all DS can be destroyed and n_s can also be well determined. $[Si^{SL}_{III}]$ is therefore the clue experimental parameter to provide both Z and W. In order to precisely obtain $[Si^{SL}_{III}]$ a higher number of samples, instead of the only three used here, would be desirable. However, in spite of the small number of samples used, valid conclusions will be drawn, because extremely high change in the value of $[Si^{SL}_{III}]$ would be necessary to invalidate them and this high change is unlikely to happen

as discussed before. Even in the case of high changes in $[Si^{SL}_{III}]$ the present approach is still valid, what will change is only the relative importance of the defect concentrations for the electrical properties.

In figure 2 we plot the three functions Z, W and An obtained using the lines for results at 77K in figure 1. The lower limit was chosen to eliminate the one to one correspondence regime, when both Z and W expression are not useful since the values of $(Si_{III} - Si_{As})$, $(Si_{III} - X)$ and (Si_{As}) are zero. For the upper limit it was supposed that only $[Si_{III}]$ has achieved his solubility limit $[Si^{SL}_{III}]$ and assumed that the linear approximation used in figure 1 should be a good one. The results depicted in figure 2 show that the dependence of W with the silicon nominal doping concentration is much stronger than the dependence of Z. We therefore conclude that the silicon atoms incorporate mainly to produce $(Si_{III} - Si_{As})$, which agrees with the conclusion based on the analysis of the ns slope. Indeed, it should be noted that for the thick line in figure 1 the slope on the right side of the solubility limit is, in absolute value, significantly smaller than that on the left side, differently from the pure GaAs case where both slopes seem to have nearly the same value[1]. The equality of the slopes indicates that the silicon atom is incorporating in the group III element on the left side and in the group V element on the right side. Otherwise, if all silicon atoms are supposed to incorporate to produce $(Si_{III} - Si_{As})$ on the right side the slope should be zero. A higher than 45° slope, in absolute value in the right side, means that defects with a state of charge smaller than -1, e.g., $[Si_{III} - X]$ are present. A simple explanation for this is that the aluminum atoms favor the formation of $(Si_{III} - Si_{As})$ in detriment of (Si_{As}) or more probably of $(Si_{III} - X)$. Actually it is not reasonable to expect a strong dependence of $[Si_{As}]$ on the aluminum content, which should, on the other hand, influence the value of $[Si_{III} - X]$, especially if the supposition that X is a gallium vacancy proves to be the correct one, so that this defect should involve
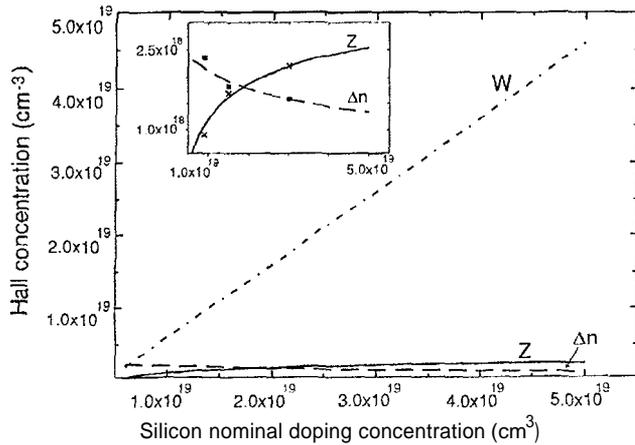
Figure 2: Two independent functions Z and W and the double ionization equation Δn. The results show that W prevails over Z and An. Tlic inset shows both Z and W in an expanded scale.
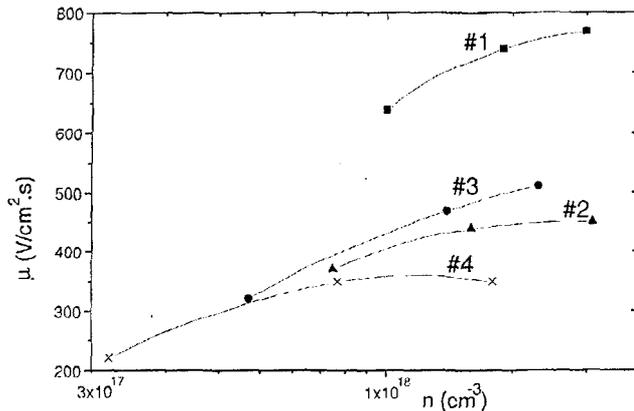
Figure 3: Hall mobilities vs. free electron concentrations, showing a inversion position for samples #2 aiid #3.

two group III element sites.

The Hall mobility versus free-electron concentration curve is shown in figure 3. Tlic results for sample #1 compare favorably with those reported in the literature, in the high doped limit. when mainly (Si_{III}) is present. There is a reduction iii the mobility values for tlie otlier three sainples which is compatible with the presence of new multiple scattering centers. The observed inversioii in position of the curves for samples #2 and #3 indicates that multiple defects are competing to form a. coniplex total scattering cross section for the electron. A simple explanation is that just beyond the $[Si_{III}^{SL}]$ solubility limit concentration the contribution to the scattering cross section comes first from one of the multiple defects, probably (Si_{As}). This contribution will then

reduce in detriment of the contribution due to other defects, probably $(Si_{III} - X)$ as the nominal silicon coiicentration is further increased. That niust be true because the negative state of charge of $(Si_{III} - X)$ is higher than tliat of (Si_{As}) turning the Coulomb interaction more effective. Later, both defect concentrations will be completely dominated by $(Si_{III} - Si_{As})$, which in turns reduce the effective scattering cross section, because it is a neutral defect,.

IV. Conclusions

The heavily silicon doped $Al_{0.3}Ga_{0.7}As$ layers grown by MBE were characterized by Hall measurements with tlie emphasis on the niultiplicity of defects. We have shown for the first time that the silicon atoms incorporation on tlie group III element sublattice yielding shallow donors and relative defect concentrations are related to the aluminum content. We obtained two equations enclosing three unknown defect concentrations. If one of them could be found using some other experimental technique, then the qiiantitative values for them can be determined. The total scattering cross section for the electrons shows a complex behavior as a function of the nominal silicon concentration, showing a local maximum which inclicates that competition phenomena are present.

Acknowledgments

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