Defects and Diffusion in Semiconductors and Heterostructures:

Non-equilibrium Defects and Diffusion in Semiconductors: III-V's

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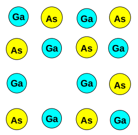
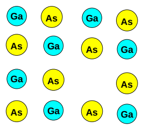
Point defects in GaAs





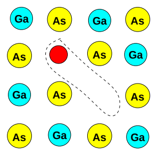
- Intrinsic defects in GaAs include both arsenic and gallium vacancies
- The concentration of vacancies is mainly determined by the overpressure of arsenic during the growth
- In addition to being neutral arsenic vacancies behave as deep donors and gallium vacancies exhibit deep acceptor-like bahaviour

Point defects in GaAs

- A number of other intrinsic defects is known to exist in GaAs
- Their nature and concentration depend on how the material is grown or treated
- Most of these can be thermally annealed out by 250 °C
- An exception is the antisite defect As_{Ga} which is stable to 950 °C

Point defects in GaAs

- Intrinsic defects can also exist in the form of complexes with other defects as well as impurities



- One such is the defect impurity complex gallium vacancy – shallow donor pair (V_{Ga}^{-}-donor), which behaves as a deep acceptor
- It occurs with all group IV and group VI shallow donors
- One consequence of this is that the free carrier concentration in $n-$type GaAs is generally less than the dopant concentration, the material is compensated

Point defects in GaAs

Defect	Distance from E_c [eV]	Distance from E_v [eV]
V_{As}	0.045	
As_i	0.5	
V_{As} - As_i	0.3	0.06
As_{Ga} - V_{As}	0.76	
	0.35	
Ga_{As}		0.077
		0.23
V_{Ga} - Si_{Ga}	1.18	
V_{Ga} - C_{Ga}	1.17	
V_{Ga} - Se_{As}	1.22	
V_{Ga} - Te_{As}	1.21	
V_{Ga} - S_{As}	1.20	

Point defects in GaAs

- Arsenic vacancy
  - V_{As}^{+} $E_c - 0.14$ eV
  - V_{As}^{-} $E_c - 0.03$ eV [Saarinen et al., 1991]
- Gallium vacancy
  - Experimental values are lacking
  - V_{Ga}^{-} $E_v + 0.13$ eV
  - V_{Ga}^{2-} $E_v + 0.49$ eV
  - V_{Ga}^{3-} $E_v - 0.98$ eV [Hurle, 1999]

Point defects in GaAs

- The isolated arsenic antisite is commonly referred to as EL2
- It forms two donor states
  - As_{Ga}^{+} $E_c - 0.75$ eV
  - As_{Ga}^{2+} $E_g - 0.54$ eV
- The native defect EL2 can be used to make GaAs semi-insulating

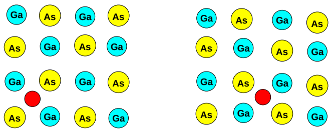
Diffusion in GaAs

- Diffusion describes the process by which atoms move in a crystal lattice
- Diffusion is a process in which impurities may be introduced in to selected regions of a semiconductor
- Diffusion is extensively used in silicon technology
- The behavior of diffusion in GaAs is more complex and less understood than in silicon and cannot be controlled as precisely

Diffusion in GaAs

The mechanism by which diffusion takes place is

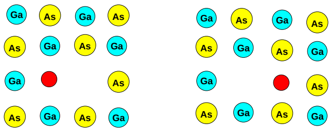
- Interstitial diffusion



  - An impurity atom jumps from one interstitial site to the next
  - This process is relatively fast because there are a number of vacant sites of this type in a semiconductor

Diffusion in GaAs

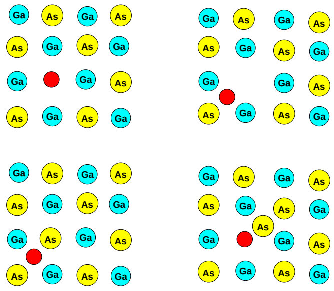
- Substitutional diffusion



  - An impurity atom wanders through the crystal by jumping from one lattice site to the next and substituting for the host atom
  - It is necessary that this adjacent site is vacant
  - Divacancies are also present in the semiconductor and their energy of formation is somewhat lower than for isolated vacancies
  - This is important diffusion mechanism in $n-$type GaAs

Diffusion in GaAs

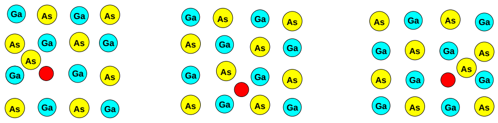
- Interstitial-substitutional diffusion



  - Impurity atoms occupy substitutional as well as interstitial sites
  - The dissociative mechanism (substitutional impurity leaves behind a vacancy) can be the controlling factor
  - The effective diffusivity depends on impurity concentration and crystal quality
  - Zinc, cadmium and copper move in GaAs by this mechanism

Diffusion in GaAs

- Interstitialcy diffusion



  - Interstitial host atoms (self-interstitials) are annihilated by pushing substitutionally located impurity atoms into interstitial site
- Combinations of these mechanism may occur within a crystal 0
  - Fraction of impurity atoms may diffuse substitutionally and the rest interstitially

Diffusion in GaAs

- Substitional diffusion is based on the interaction of the impurity ion with vacancies in the zincblende lattice
- The charge state of these vacancies can strongly influence the nature of this interaction and thus the effective diffusivity
- In general all deep levels can exhibit one or more different charge states
- Vacancies can thus be represented by

$$\mathrm{V}^{+}, \mathrm{V}^{0}, \mathrm{V}^{-}, \mathrm{V}^{2-}, \mathrm{V}^{3-}, ...$$

- These vacancies will interact with the diffusing impurity in different ways

Diffusion in GaAs

- For a small amount of impurity A diffusing in semiconductor lattice, the diffusion is characterized by intrinsic diffusivities, $D_i^0, D_i^+, D_i^-, D_i^{2-}, D_i^{3-}, ...$, associated with $\mathrm{A}-\mathrm{V}^0, \mathrm{A}-\mathrm{V}^+, \mathrm{A}-\mathrm{V}^-, \mathrm{A}-\mathrm{V}^{2-}, \mathrm{A}-\mathrm{V}^{3-}, ...$ pair interaction, respectively
- The diffusion in an extrinsic semiconductor is characterized by

$$D = D_i^0 + D_i^+\left(\frac{p}{n_i}\right) + D_i^-\left(\frac{n}{n_i}\right) + D_i^{2-}\left(\frac{n}{n_i}\right)^2 + D_i^{3-}\left(\frac{n}{n_i}\right)^3 + ...$$

- In GaAs this is more complex due to the possibility of defect interaction with the vacancies and interstitials of both gallium and arsenic
- Thus a general form of the above equation involving four sets of terms is required

Diffusion in GaAs

- Extensive studies have not been made on the diffusion of impurities in GaAs
- The diffusion of gallium and arsenic in GaAs follows:

$$D_{\mathrm{Ga}} = 0.1 \times \exp(-3.2/kT) \qquad \mathrm{cm}^2/\mathrm{s}$$

$$D_{\mathrm{As}} = 0.7 \times \exp(-5.6/kT) \qquad \mathrm{cm}^2/\mathrm{s}$$

- These different rates indicate that self-diffusion of gallium and arsenic occurs along separate sublattices, with each atom moving in its own sublattice
- Typically, impurities from group II (Cd, Zn, Hg) are shallow and $p-$type and move along the gallium sublattice
- But substitutional diffusion alone cannot accomplish this, since each gallium has four arsenic neighbors
- These impurities thus have to move with an interstitial-substitutional mechanism

Diffusion in GaAs

- Impurities from group VI (Se, S, Te) are shallow and $n-$type
- They are believed to diffuse by a divacancy mechanism
- This is similar to substitutional behavior so these impurities are extremely slow diffusers
- Impurities from group IV (C, Ge, Si) can be either $n-$type or $p-$type, depending on the sublattice on which they are preferentially located
- It is generally assumed they move on both sublattices, but no detailed diffusion model has been proposed
- It is common to list the diffusion data in the Arrhenius form

$$D = D_0 \times \exp(-E_{\mathrm{d}}/kT)$$

Diffusion in GaAs

- Silicon is an important dopant for $n-$type GaAs
- This is due to the fact that it is relatively easy to anneal the silicon implants
- Diffusion of silicon during annealing can be approximated by

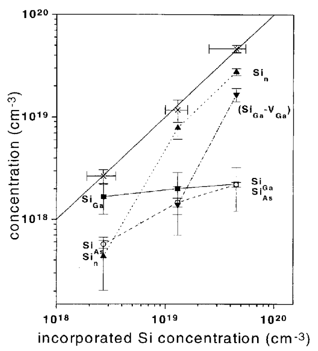
$$D_{\text{eff}} = D_i^{2-} \times \left(\frac{n}{n_i}\right)^2$$

$$\approx 60.1 \times \exp(-3.9/kT) \left(\frac{n}{n_i}\right)^2 \quad \text{cm}^2/\text{s}$$

- Interaction with the gallium vacancy V_{Ga}^{2-} is thus assumed to be the primary diffusional mechanism
- Others have proposed interactions with V_{Ga}^{3-} to be dominant

Diffusion in GaAs

- In highly doped n-GaAs the free electron concentration tends to saturate with increasing silicon dopant concentration

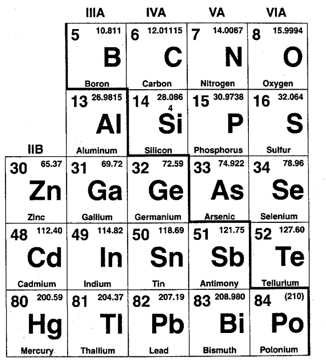


[Domke et al., 1996]

Diffusion in GaAs

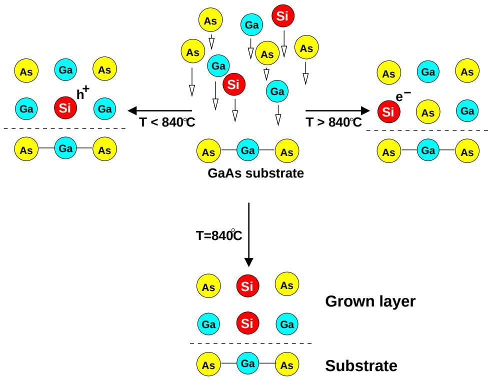
- Thus the diffusion and defect formation in GaAs is not properly understood
- Let's look at two examples:
  - Annealing of Si doped GaAs
  - Annealing of Li diffused GaAs

Annealing of Si doped GaAs



- Si is a group IV element and can therefore result in either $p-$ or $n-$type behavior in GaAs, depending on whether it occupies As or Ga site
- Such behavior is called **ampotheric**

Annealing of Si doped GaAs



- At high growth temperatures Si–doped GaAs samples grown by liquid–phase–epitaxy (LPE) are n–type while at lower growth temperatures they are p–type

Annealing of Si doped GaAs

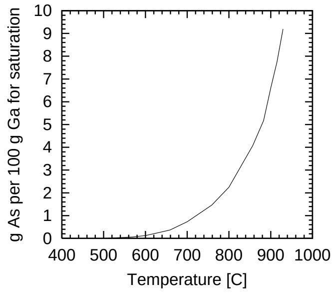
- The actual crossover temperature depends on silicon concentration and crystal orientation [Ghandhi, 1994]
- This implies that Si–doped LPE is always compensated to some degree and the concentration of $\mathrm{Si_{Ga}}$ and $\mathrm{Si_{As}}$ should be of similar order
- Gallium arsenide grown by LPE from gallium melt is expected to be low in gallium vacancies and possibly high in arsenic vacancies [Milnes, 1983]
- Under these conditions Si should predominantly be a shallow acceptor on As site as well as a shallow donor on Ga site

Annealing of Si doped GaAs

- In n-type GaAs at low doping level the Si atoms predominantly occupy Ga lattice sites but a smaller fraction occupies As sites as acceptors
- At higher doping levels $\mathrm{Si_{Ga}}$-$\mathrm{V_{Ga}}$ pairs and possibly a $\mathrm{V_{Ga}}$-$\mathrm{Si_{As}}$-$\mathrm{As_{Ga}}$ complex are present
- Ashwin et al. [Ashwin et al., 1994] report that only one type of acceptor $\mathrm{Si_{Ga}}$ was present in as grown LPE GaAs
- Growth at high temperatures evidently favors Si on Ga sites and the material becomes p-type

Annealing of Si doped GaAs

- This can be understood by looking at the solubility curve of As in Ga melt



- The solubility of As rises rapidly above 500 °C
- Increased [As] lower the arsenic vacancy concentration [$\mathrm{V_{As}}$] and consequently the available As sites for Si–atoms

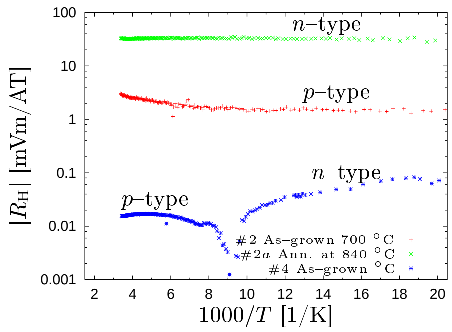
Annealing of Si doped GaAs

- The ratio [As]/[Si] in the melt is increased by increased temperature so the available As sites will be occupied faster by As while the concentration ratio [Ga]/[Si] in the melt is constant
- If the [As] is increased sufficiently while the [Ga] is fixed, then the formation rate of $[\mathrm{Si_{Ga}}]$ will eventually exceed the rate of formation of $[\mathrm{Si_{As}}]$
- A deep donor gallium–vacancies complex, $[\mathrm{Si_{Ga}}-\mathrm{V_{Ga}}]$, partially autocompensates all donor–dopant regardless of growth temperature

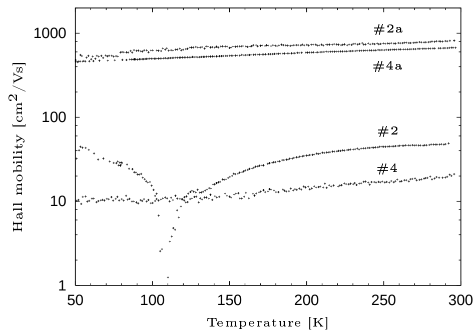
Annealing of Si doped GaAs

- GaAs films were grown by liquid phase epitaxy on a semi–insulating GaAs (100) substrate
- Four LPE batches were made. Two of which were grown at temperatures around 700 °C and the other two at 840 °C
- One batch of each temperature was grown with low Si concentration in the melt ($\sim 10^2$ ppm) and the other with high Si concentration ($> 10^3$ ppm)
- One piece of each of the four LPE batches was baked in quartz ampoules at 840 °C in As gas pressure of several hundreds millibars at the baking temperature for 24 h, with a subsequent quenching in liquid nitrogen

Annealing of Si doped GaAs



Sample #2, grown at 700 °C, is p-type and after annealing it becomes n-type with roughly an order of magnitude higher Hall mobility (sample #2a). The highly doped sample #4 grown at 840 °C, exhibits p-type behavior at elevated temperatures but n-type behavior below 105 K. A Hall overshoot is apparent at $p = n(\mu_n/\mu_p)^2$ where the electrons and holes attempt to cancel the contributions of each other towards the Hall effect



The Hall mobility of high Si–doped GaAs as a function of temperatures. Sample #2 is p-type GaAs, as-grown at 700 °C; #2a is n-type GaAs, grown at 700 °C and annealed at 840 °C; #4 is GaAs as-grown at 840 °C and is n-type below 105 K; #4a is n-type GaAs grown at 840 °C and annealed at 840 °C.

Table I: The carrier concentration, mobility and conductivity obtained by Hall measurements at room temperature and PL peak shift with excitation intensity measured at 14 K in as–grown and annealed samples.

Sample	Carrier concentration $[\mathrm{cm}^{-3}]$	$[\mathrm{Si}]_{\mathrm{tot}}$ $[\mathrm{cm}^{-3}]$	$R_{\mathrm{n/p}}$ * $[\frac{\mathrm{cm}^{-3}}{\mathrm{cm}^{-3}}]$	$[\mathrm{Si}]_{\mathrm{gs}}$ ** $[\frac{\mathrm{mg(Si)}}{\mathrm{g(Ga)}}]$	Shift $[\frac{\mathrm{meV}}{\mathrm{decade}}]$	Mobility $[\frac{\mathrm{cm}^2}{\mathrm{Vs}}]$
		Low Si–doping level				
#1	$p = 1.6 \times 10^{17}$	1.0×10^{18}	0.72	0.11	6	110
#1a	$n = 3.9 \times 10^{17}$	1.0×10^{18}	0.44	0.11	2–5	880
#3	$n = 2.3 \times 10^{16}$	2.5×10^{17}	0.83	0.04	8	2500
#3a	$n = 1.9 \times 10^{17}$	2.5×10^{17}	0.24	0.04	0–1	2900
		High Si–doping level				
#2	$p = 4.0 \times 10^{18}$	1.5×10^{19}	0.58	2.1	5	20
#2a	$n = 3.8 \times 10^{17}$	1.5×10^{19}	0.95	2.1	24	820
#4	$p = 3.5 \times 10^{17}$	7.0×10^{18}	0.90	1.3	8	50
#4a	$n = 9.1 \times 10^{16}$	7.0×10^{18}	0.97	1.3	15	670

**$[\mathrm{Si}]_{\mathrm{gs}}$ = silicon concentration in growth solution.

Annealing of Si doped GaAs

- The compensation was either increased or decreased by the annealing, depending on the dopant concentration
- Annealing of the highly doped samples, #2 and #4, increased the compensation ratio from 0.58 to 0.90 and from 0.95 to 0.98, respectively.
- In the less doped samples #1 and #3 the annealing lowered the compensation, from 0.72 to 0.44 and 0.83 to 0.24, respectively.

Annealing of Si doped GaAs

- The annealing of p-type samples converted them into n-type with ~ 10 times higher mobility
- Our results strongly suggest that the type conversion from p– to n–type may in fact be caused by such site switching.

Annealing Li diffused GaAs

- The electrical behavior of lithium in GaAs has been studied extensively in the past primarily by Fuller and coworkers [Fuller and Wolfstirn, 1962, Fuller and Allison, 1964]
- Lithium has, like hydrogen, a tendency to form complexes with other impurities and native defects when migrating in crystals
- It is known that Li diffusion into GaAs reduces the free carrier concentration which leads to electrical resistivity as high as 10^7 Ω cm in undoped, n-type and p-type starting materials [Gíslason et al., 1992]
- It has been suggested that lithium passivates shallow acceptors in GaAs but compensates shallow donors [Yang et al., 1993].

Annealing Li diffused GaAs

- Passivation of electrically active defects in semiconductors is characterized by a simultaneous reduction of carrier concentration and increase of carrier mobility
- This is due to the formation of neutral pairs that reduces the carrier concentration as well as the number of ionized scattering centers
- It has been demonstrated that annealing of Li diffused GaAs at 400 – 500 °C in pure Ga or Ar atmosphere reduces the Li concentration by about two orders of magnitude [Fuller and Allison, 1964, Yang et al., 1993]
- This out-diffusion of Li produces p-type material

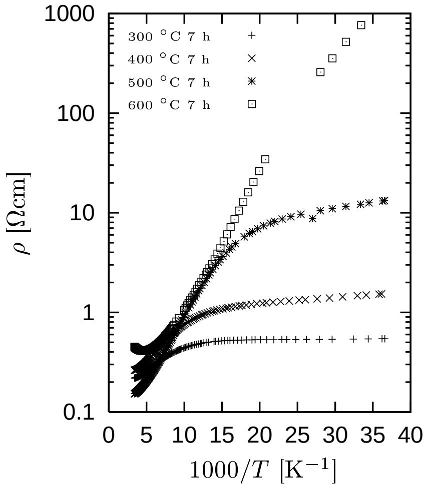
Annealing Li diffused GaAs

- This phenomenon was first reported by Fuller and Wolfstirn [Fuller and Wolfstirn, 1962] but the mechanism responsible for the conductivity change has not been fully identified
- The resulting p-type conductivity indicates formation of acceptors which have earlier been related to gallium vacancy [Yang et al., 1993, Gislason et al., 1997].
- It has been suggested that doping GaAs with lithium at high temperature (700 – 800 °C) increases the concentration of both the gallium vacancy V_{Ga} and the gallium antisite Ga_{As} [Gislason et al., 1997]

Annealing Li diffused GaAs

- Positron annihilation spectroscopy shows that both gallium vacancy (V_{Ga}) and the gallium antisite defects (Ga_{As}) are formed during the diffusion of Li and increase in concentration upon out-diffusion of Li (annealing) [Arpiainen et al., 1999]
- It has been suggested that the majority of V_{Ga} and Ga_{As} defects is formed during the diffusion phase at 800 °C but remain passivated until out diffusion at > 400 °C [Arpiainen et al., 1999]
- The arsenic antisite As_{Ga} (EL2) and As vacancy V_{As} defects are not detected after the incorporation of Li [Arpiainen et al., 1999]

Annealing Li diffused GaAs



- The figure shows a semilogarithmic plot of the resistivity ρ versus $1000/T$ for GaAs:Si diffused with lithium at 800 °C and baked at various temperatures

Annealing Li diffused GaAs

- The resistivity increases with increased annealing temperature
- The room temperature resistivity after lithium diffusion is $\rho = 1.3 \times 10^5\ \Omega$cm, but varies from 0.04 – 0.2 Ω cm while varying the annealing temperature from 600 °C to 300 °C
- For the sample annealed at 600 °C for 7 h the conduction is activated with an activation energy $E_{A0} \approx 25$ meV over the entire temperature range, consistent with Fuller and Allison [Fuller and Allison, 1964]
- For the samples annealed at 300 °C – 500 °C the slope of the resistivity curve becomes much shallover below 100 K and hopping conduction is evidently dominant

Other examples

- The decrease in resistivity of GaAs when irradiated by neutrons at high fluences 10^{17} – 10^{20} n/cm^2 has been explained by variable-hopping conduction between defect clusters involving isolated As_{Ga} defects [Coates and Mitchell, 1972, Satoh and Kuriyama, 1989]
- Furthermore variable-range-hopping is known to exist in MBE GaAs grown at very low temperatures [Look et al., 1994, Betko et al., 1996, Morvic et al., 1998].

Summary

- The diffusion mechanism in GaAs is not fully understood
- We demonstrated site switching of Si in GaAs by annealing
- We see hopping conductivity in Li diffused and annealed GaAs
- In both of these examples vacancies play a key role

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