CHAPTER 6

PREVIOUSLY PUBLISHED RESULTS

Over the last 100 years many investigations were done on diffusion in solids to understand the mechanisms that are involved in this process. Specialised conferences on diffusion were held for researchers to exchange their latest knowledge (for example: Diffusion in Materials 'DIMAT 96').

For this study the diffusion behaviour of aluminium in five different semiconductors was investigated. The investigated semiconductors can be summarised in two groups: elemental semiconductors (silicon and germanium) and *III-V* compound semiconductors (gallium arsenide, indium phosphide and indium antimonide).

Publications of the investigated systems are mentioned in this review as well as work on related or similar systems. Aluminium diffusion coefficients in indium phosphide and indium antimonide were not found in the literature.

6.1. ELEMENTAL SEMICONDUCTORS

An important summary on diffusion in silicon and germanium is a review article by *Seeger* and *Chik* [8]. Although this article was written in 1968 the major diffusion mechanisms and self-diffusion coefficients in these semiconductors are discussed. An extensive reference list concludes this review. The diffusion mechanisms mentioned in this review are discussed in chapter 2.2.1.

Recent research was done on implantation of impurities (dopants) followed by successive annealing to diffuse them onto a desired lattice site for electrical activation.

6.1.1. SILICON

A large amount of publications in the past 20 years is dealing with aluminium in silicon. This list can only give an overview and cannot claim to be complete.

The aluminium-silicon system is a simple eutectic system with two solid solution phases, fcc (aluminium) and diamond cubic (silicon) [55]. The maximum solubility of silicon in aluminium is found to be 1.5 ± 0.1 at.% at the eutectic temperature, and decreases to 0.05 at.% at 300 °C. The maximum solubility of aluminium in silicon is only 0.016 ± 0.003 at.% at 1190 °C, the retrograde point of the silicon solidus. Aluminium - silicon alloys have not been reported to form metastable intermetallic compounds or glassy alloys.

Some of the results on aluminium diffusion in silicon are summarised in ref. [56] including a list of diffusion coefficients and their references. The interest of aluminium as an impurity arises from the fact that it diffuses faster than other group *III* acceptors.

The diffusion coefficients found were subject to controversy because differences of up to two orders of magnitude were found.

D_0 [$cm^2\ s^{-1}$]	E_A [eV]	D (900 °C) [$10^{-15}\ cm^2\ s^{-1}$]	References
8	3.47	9.64	*Fuller, Ditzenberger* [57]
2800	3.9	128	*Goldstein* [58]
4.8	3.36	17.2	*Miller, Savage* [59]
0.5	3.0	63.2	*Kao* [60]
1.38	3.41	3.01	*Ghoshtagore* [61]
1.8	3.2	31.4	*Rosnowski* [62]
8.88	3.44	14.4	*Galvagno* [63]
7.40	3.42	15	*La Ferla* [64]

Table 2: Pre-exponential factors and activation energies in $D = D_0 \exp(-E_A / kT)$ quoted by different authors. The diffusion constant at 900 °C is given for the purpose of comparison.

The differences seen in table 2 are largely due to the nature of the impurity sources and diffusion conditions. In ref. [57] aluminium metal in an evacuated tube was used to deposit a film of aluminium onto silicon. The diffusion coefficient was measured using the *p-n*-junction method (see chapter 2.3). The lowest annealing temperature was 1085 °C for 234

hours. In ref. [58] an aluminium - silicon alloy button was placed on top of the silicon substrate within an evacuated tube. In ref. [59] the substrate and source were placed inside a silicon boat held within a tantalum tube which acted as a getter to avoid any reaction between the quartz tube and the substrate. This assembly was heated in an open arrangement under helium or argon gas flow. *Ghoshtagore* [61] diffused aluminium into Si <111> from doped epitaxially deposited source layers in a floating hydrogen atmosphere. The temperature dependence of the intrinsic diffusion coefficient was obtained above 1120 °C. *Rosnowski* [62] uses a high vacuum, open tube method for aluminium diffusion into silicon. The diffusion coefficient was determined in the temperature range 1025 –1175 °C.

Galvagno et al. [63] implanted a low dose (1 x 10^{14} cm^{-2}) aluminium ions at 80 *keV*, 300 *keV* and 6 *MeV*. The annealing temperature range was from 1000 °C - 1290 °C using rapid thermal processes in a nitrogen atmosphere for a few seconds and in a SiC tube furnace for longer times up to 16 hours. The depth profiles were obtained using SIMS. The aluminium dose lost through the surface was taken into account. It was concluded that SiO_2 is not a suitable capping layer to prevent loss of aluminium due to the reaction of aluminium with oxygen to form Al_2O_3. Aluminium arriving at the SiO_2 / Si interface is lost in Al_2O_3 precipitates and the range of aluminium in silicon is shifted towards the silicon surface.

To avoid surface effects aluminium was implanted with 100 *MeV* into CZ and FZ silicon substrates [64]. The natural oxygen content in CZ and FZ silicon was determined to be $\approx 10^{16}$ cm^{-3} and $\approx 10^{17}$ cm^{-3}, respectively The annealing temperature was 1200 °C at different annealing times. SIMS analysis apparently revealed a multipeak structure of O and Al around the projected range of Al. The results imply that the Al-O complex formation is enhanced by the presence of oxygen but that it is catalysed by the damage created during the implantation.

Bruesch et al. [76] implanted 3 x 10^{15} aluminium ions cm^{-2} at an energy of 150 *keV*. A maximum concentration at 218 *nm* with a range straggling value of 69 *nm*, determined with SIMS was obtained after implantation. The out-diffusion after annealing was determined. It was found that only 8% of the aluminium atoms remain in the sample. The rest (92%) was lost by out-diffusion. Annealing temperatures were 1060 °C for 10 min (rapid thermal annealing - *RTA*) in vacuum. The formation of Al_2O_3 precipitates was observed at a depth of 350 *nm* after annealing. This depth corresponds to the position of the interface between

damaged and undamaged region in the crystal. The oxygen for the formation of complexes is either present in the wafer or is coming from the residual gas. The precipitates consist of platelets lying on a well-defined lattice plane. Two types with orientation 90° to each other lying in the (110) plane are observed. A second row of small precipitates was observed in some areas of the specimen at a depth of 230 nm. These precipitates reveal no crystalline structure and are less than 6 nm in diameter. Their structure could not be clearly analysed. The determined aluminium diffusion constant D at 1333 K ranges between 1.7 x 10^{-13} and 1.6 x 10^{-11} $cm^2\ s^{-1}$, which is close to the value $D = 1.2 \times 10^{-11}\ cm^2\ s^{-1}$ measured by Goldstein [58] at this temperature.

Annealing temperatures ≥ 1200 °C of aluminium implanted (FZ) Si <111> were used to investigate aluminium precipitates [66]. For this study 1 x 10^{15} aluminium ions cm^{-2} were implanted at an energy of 150 *keV*. Annealing took place in nitrogen atmosphere. Different capping layers were applied to prevent the loss of aluminium atoms. The observed precipitates were found to have a crystalline structure after annealing.

Ref. [67] reports on 3 x 10^{15} aluminium ions cm^{-2} that were implanted at an energy of 60 *keV*. Back-diffusion by using different capping layers was investigated. Annealing temperatures were 900 - 1250 °C for 1 hour and up to 16 hours in a nitrogen ambient. It was found that aluminium precipitates may be formed at temperatures as low as 350 °C in the damaged region induced by aluminium implantation. These precipitates are stable below 900 °C.

The latest study on this system was done by *Kuhlmann* et al. [68] (see figure 17). The diffusion of aluminium in silicon and its interaction with phosphorus and boron has been investigated. The aluminium predeposition was carried out in vacuum using a silicon sandwich structure consisting of a silicon-target wafer and a source wafer, which was covered by a 300 *nm* aluminium film. Additional results for the aluminium in-diffusion were obtained by annealing predeposited samples without the diffusion source (drive-in). The depth profiles before and after RTA (rapid thermal annealing) were characterised by SIMS. Additionally a big change in the aluminium diffusion behaviour in the presence of boron or phosphorus was observed. A supersaturation of self-interstitials caused by a high surface concentration of boron or phosphorus leads to an accelerated aluminium diffusion in Si <111>. The authors assume that aluminium migrates as a negative ion in silicon and that it uses self-interstitials as

diffusion vehicles. The annealing temperatures used were, like in most of the other reported results, higher than 1000 °C.

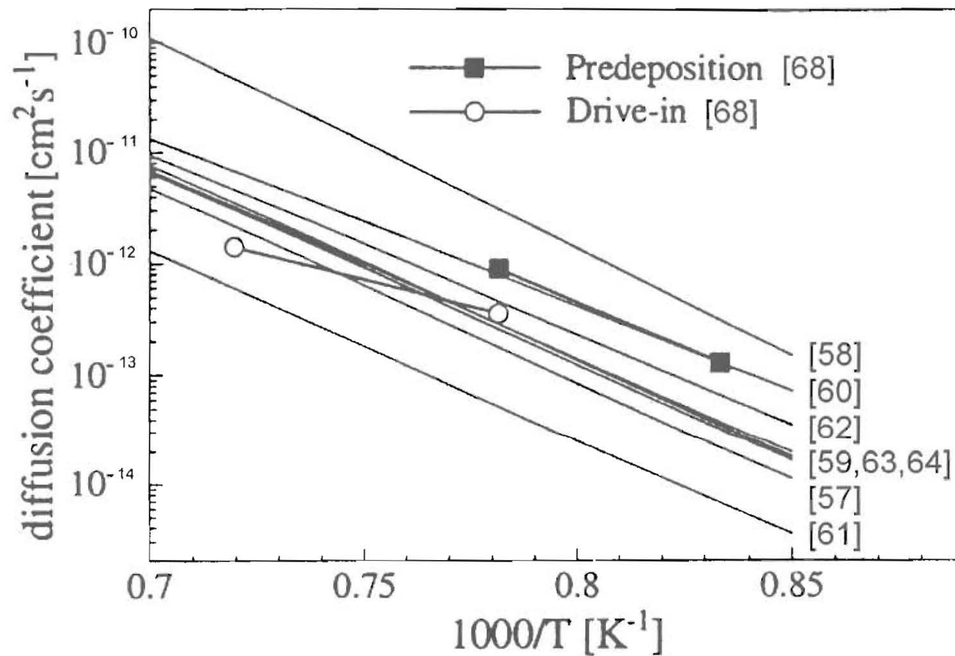

Fig.17: Diffusion coefficients of aluminium with bibliographical reference [68].

Recent publications dealing with aluminium implantations at elevated substrate temperatures were not found. The only previously reported work [69] of aluminium implanted into heated FZ – Si <111> substrates to avoid radiation defects dates back to 1969. Out-diffusion was observed after annealing the room temperature implanted samples, however an explicit analysis for diffusion coefficients was not performed.

A wide spread of the published results over the past years is evident. An extrapolation of the reported data in table 2 and fig. 17 results in an expected diffusion coefficient between 3 x 10^{-15} cm^2 s^{-1} and 1.3 x 10^{-13} cm^2 s^{-1} for T_a = 900 °C. An average of D_0 = 354 cm^2 s^{-1} is calculated for the pre-exponential factor with an average activation energy of E_A = 3.4 eV. The average diffusion coefficient at 900 °C is calculated to be D = 4 x 10^{-14} cm^2 s^{-1}. The main reasons for this spread over two orders of magnitude are different analysing methods and different diffusant sources as well as other factors like point or extended defects. All the reported results were done on only one diffusant source.

For an annealing temperature of T_a = 900 °C the previously reported results are in the detection range of our method. Therefore, investigations on different diffusant sources as well as radiation induced lattice defects and their influence on the diffusion coefficient were done in this work and compared with previously reported results.

6.1.2. GERMANIUM

The maximum solubility of aluminium in germanium is 1.09 at.% at an eutectic temperature of about 420 °C [70].

In *Seeger* and *Chik*'s review in 1968 [8] on diffusion of different elements in germanium and silicon no values for diffusion coefficients of aluminium in germanium were listed.

The diffusion coefficient of aluminium in germanium was reported by ref. [71]. Thin aluminium layers (5-28 *nm*) were deposited onto clean germanium crystals. Samples were annealed in vacuum from 827 *K* up to 1178 *K* and the diffusion behaviour was analysed with SIMS. An activation energy $E_A = 3.45 \pm 0.04$ *eV* and a pre-exponential factor $D_0 = (1.0 \pm 0.5) \times 10^3\ cm^2\ s^{-1}$ was obtained for the diffusion coefficient of aluminium in germanium.

The only other work on this system was reported in 1967 by ref. [72] who used sheet resistance measurements. Annealing temperatures ranged from 1023 K up to 1123 K and resulted in an activation energy of $E_A = 3.24$ *eV* and a pre-exponential factor $D_0 = 160\ cm^2\ s^{-1}$.

The reported results on aluminium diffusion in germanium by *Dorner* [71] and *Meer* [72] calculate to $D_{[71]} = 1.1 \times 10^{-15}\ cm^2\ s^{-1}$ and $D_{[72]} = 2.2 \times 10^{-15}\ cm^2\ s^{-1}$ at a temperature of T_a = 700 °C and to $D_{[71]} = 3 \times 10^{-20}\ cm^2\ s^{-1}$ and $D_{[72]} = 1 \times 10^{-19}\ cm^2\ s^{-1}$ at a temperature of T_a = 500 °C.

The previously reported diffusion coefficients at T = 700 °C vary by a factor of two. They are in the range that can be detected with our method. Therefore, the measurements performed in this work are to verify which of the two reported results can be relied on at T_a = 700 °C.

6.2. COMPOUND SEMICONDUCTORS

The compound semiconductors in this work gallium arsenide, indium phosphide and indium antimonide are all combinations of group *III* elements with group *V* elements. These *III-V* semiconductors have the zincblende crystal structure, in which each group *III* atom has four group *V* atoms as nearest neighbours, and vice versa. Most of the *III-V* semiconductors can be produced as large bulk crystals, but only gallium arsenide and indium phosphide are currently made in larger quantities. The two major methods of growth are the horizontal Bridgeman and the Czochralski techniques.
Impurity diffusion analysis in compound semiconductors is more complicated than in elemental semiconductors because of the fact that three elements have to be considered. The impurity could occupy a substitutional site of the group *III* element or of the group *V* element.

A basic review on ion implantation applied in *III-V* semiconductors is summarised in ref. [19], however, without including aluminium ions. The introduced damage during implantation and annealing methods in indium phosphide, gallium arsenide and some other compounds (not indium antimonide) is discussed there.

Because of the zincblende structure six different single point defects have to be considered in *III-V* compounds: vacancies in the group *III* – sub-sublattice, vacancies in the group *V* - sub-lattice, group *III* - self-interstitials, group *V* - self-interstitials and antisite defects e.g. group *III* atoms on group *V* sites or of group *V* atoms on group *III* sites.

6.2.1. GALLIUM ARSENIDE

A review of recent developments in the understanding of self- and impurity diffusion processes in gallium arsenide can be found in ref. [73]. For a consistent description of the diffusion processes involved in gallium arsenide one has to know the intrinsic point defects involved in the diffusion in both sublattices. Fig. 18 summarises the results from this review with a list of the different authors and years.

Aluminium is a group *III* element and can therefore also be used with other group *V* elements to form a *III-V* compound semiconductors. As all *III – V* semiconductors have a zincblende

structure the possibility of epitaxial growth of one compound onto another arises. The difficulty here is the different lattice constant. However, some compounds are compatible for this procedure like for example gallium arsenide and aluminium arsenide. Inter-diffusion between gallium arsenide and aluminium arsenide, more precisely, the inter-diffusion between gallium and aluminium was studied by *Chang* and *Koma* [74]. The objects of their study were multilayer heterostructures of the type GaAs - AlAs - GaAs or $Al_xGa_{1-x}As$ - $Al_xGa_{1-x}As$ - ...... ($0 \leq x \leq 1$)grown by molecular beam epitaxy (*MBE*). The thickness and composition of each layer was monitored. The gallium arsenide and aluminium arsenide layers had identical thicknesses of about 0.155 μm. The diffusion anneal was carried out in the temperature range 850 - 1100 °C in vacuum with an arsenic source in the ampoule to provide an overpressure for the protection of the sample surface. Depth and composition profiles after annealing were obtained with Auger-electron spectroscopy (AES). The diffusion coefficient obtained can be empirically represented by a single modified Arrhenius expression, $D(x,T) = D_0 . \exp(-E_A(x) / kT)$, where the pre-exponential factor is given by $D_0(x)=92 \exp(-8.2x)$ (in $cm^2\ s^{-1}$) and the activation energy of diffusion $E_A(x)=4.3-0.7x$ (in eV). The Al-Ga inter-diffusion data approximate those for Ga self-diffusion closely, because the Al diffusivity in GaAs is very close to that of Ga. Therefore symbols for Ga-Al interdiffusion and for Ga self-diffusion D_{Ga} are used interchangeably.

Schlesinger and *Kuech* [75] have employed photoluminescence spectroscopy to determine the temperature dependence of the interdiffusion coefficient of aluminium and gallium in $GaAs/Al_{0.3}Ga_{0.7}As$ quantum wells. Structures were grown consisting of alternating layers with a thickness of GaAs in the range of 20-150 Å, while the two cladding layers of $Al_{0.3}Ga_{0.7}As$ were 500 Å. The slices were subjected to heat treatments over a temperature range of 650 - 910 °C for times between one and six hours. The results obtained for interdiffusion coefficients between aluminium and gallium were an activation energy $E_A \approx 6\ eV$ and a value for $D = 4 \times 10^{-19}\ cm^2\ s^{-1}$ at 850 °C which results in a pre-exponential factor of $D_0 = 3.2 \times 10^8$ $cm^2\ s^{-1}$.

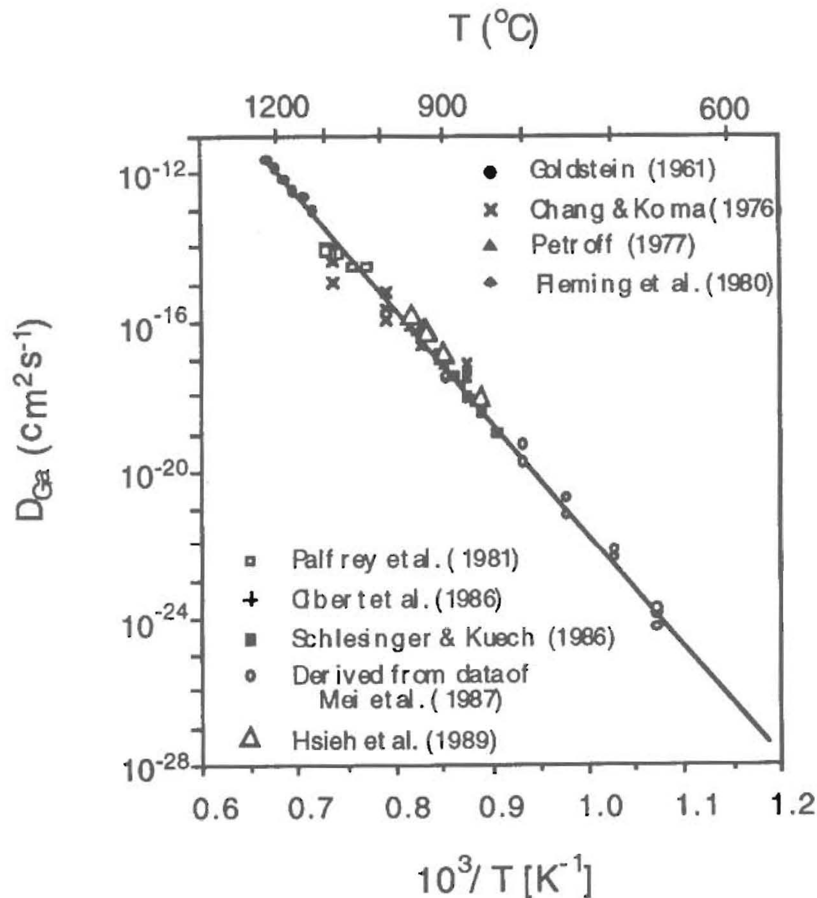

Fig.18: Self diffusion data of gallium and interdiffusion data of gallium / aluminium (open circles) in gallium arsenide as a function of reciprocal temperature [73].

Mei et al. [76] analysed the superlattice mixing of AlAs-GaAs as a function of silicon concentration. Silicon, introduced by MBE, was found to enhance the usually small diffusion coefficients of aluminium in gallium arsenide. Thermal anneals were performed in the temperature range 500-900 °C. An activation energy for aluminium diffusion in gallium arsenide of $E_A \approx 4\ eV$ was extracted. It was also found that the diffusion coefficient of aluminium was increased with increasing silicon doping concentration. The value for the activation energy of $E_A \approx 4\ eV$ in the temperature range between 800 and 1225 °C was confirmed by *Wang* et al. in ref. [77] by investigating the self-diffusion coefficient of gallium in gallium arsenide.

Goldstein [78] in 1961 was one of the first to analyse self diffusion in gallium arsenide using radio tracers. His results for the activation energy were $E_A = 5.6\ eV$ and for the pre-exponential factor $D_0 = 1 \times 10^7\ cm^2\ s^{-1}$.

Petroff [79] analysed the interdiffusion at GaAs / AlAs interfaces using transmission electron microscopy (TEM). The resulting interdiffusion coefficient D for aluminium and gallium at a temperature $T = 850$ °C is $5 \times 10^{-19} \leq D \leq 8.9 \times 10^{-19}\ cm^2\ s^{-1}$ without determining the activation energy E_A or the pre-exponential factor D_0.

Fleming et al. [80] studied the interdiffusion of aluminium and gallium in superlattices with X-ray diffraction analysis. The average diffusion coefficient for gallium and aluminium interdiffusion at 800 °C was reported to be $D = 5.3 \times 10^{-21}\ cm^2\ s^{-1}$ without determining the activation energy E_A or the pre-exponential factor D_0.

Palfrey et al. [81] studied the self-diffusion of gallium in gallium arsenide in the temperature range 1100 - 1025 °C using radiotracer techniques. An activation energy in the order of $E_A = 2.6 \pm 0.5\ eV$ and a pre-exponential factor of $D_0 = 4 \times 10^{-5} \pm 16 \times 10^{-5}\ cm^2\ s^{-1}$ were obtained. Diffusion coefficients in the above mentioned temperature range were from $D = 3 \times 10^{-15}\ cm^2\ s^{-1}$ to $9 \times 10^{-15}\ cm^2\ s^{-1}$.

A review on point defects, diffusion mechanisms and superlattice disordering in gallium arsenide based materials is summarised by ref. [82]. To determine the diffusion mechanisms in gallium arsenide and related materials, experimental results must be interpreted in association with the effects of (1) doping, (2) the group V vapour pressure and (3) point defect non-equilibrium concentrations, which may be induced by a chemical or a physical process. Gallium self-diffusion and gallium - aluminium inter-diffusion under intrinsic conditions are governed by the triply negatively charged group III sublattice vacancies V_{Ga}^{3-}. The layer disordering reaction proceeds via gallium - aluminium interdiffusion, which is immeasurable at 600 °C.

All the above-described results are consistent. A diffusion coefficient of $D \approx 10^{-30}\ cm^2\ s^{-1}$ is expected for an annealing temperature at $T_a = 500$ °C which is much lower than our detection

limit. However, a huge influence of radiation induced defects on the diffusion behaviour was observed after high dose implantation into elemental semiconductors. It is of interest to investigate if such an influence on the diffusion coefficient can be observed in gallium arsenide e.g. if a detectable aluminium diffusion after annealing occurs in samples that were implanted at *RT* and at T_i = 250 °C at a high dose. The obtained diffusion results are compared with those obtained for the in-diffusion analysis.

6.2.2. INDIUM PHOSPHIDE

Aluminium diffusion coefficients as well as implantation of aluminium in indium phosphide were not found in previously reported results. Other isoelectronic impurities, e.g. impurities with the same electron shell configuration as indium or phosphorous (boron, nitrogen, phosphorous, arsenic, antimony and bismuth) were implanted in InP [83], however, without reporting diffusion coefficients.

The scope of this work is the investigation of the diffusion behaviour of aluminium in indium phosphide for temperatures up to T_a = 400 °C by NRA. Higher annealing temperatures were not applied to avoid surface oxidation, e.g. formation of In_2O_3, which was even observed in a N_2 ambient after annealing at T_a = 450 °C [84]. The diffusion sources in this work were deposited aluminium layers and aluminium implanted at *RT* and at 250 °C.

6.2.3.INDIUM ANTIMONIDE

Aluminium implantations as well as the diffusion coefficients of aluminium in indium antimonide were not found in previously reported results. Therefore these measurements were performed to investigate the diffusion behaviour of aluminium in indium antimonide.

Bulk indium antimonide is a well-established material for high quality thermal imaging in the 3-5 μm wavelength range. With the lowest band gap (E_g = 0.16 *eV* at *T* = 300 *K*) of any binary *III-V* semiconductor material, it exhibits a very low electron effective mass and high mobility [85].

The surface of an implanted indium antimonide is chemically very active. Oxide films form when exposed to atmosphere after high dose implantations of heavy ions [86]. Irradiation damage was investigated by nitrogen implantation at an energy of 150 keV [87]. During the irradiation the crystal structure was monitored with channeling methods. An irreversible degradation of the single-crystal properties in indium antimonide was observed for doses that exceeded (3-5) x 10^{15} ions cm^{-2}.

Another problem is the swelling of ion implanted indium antimonide, which was investigated by ref. [88]. Phosphorus, arsenic and nitrogen were implanted at different energies and different doses into indium antimonide that was partly masked. The swelling of the substrate between the masked and unmasked area was dependent on the implanted dose and was only observed for ions heavier than mass $m \approx 12$. The swelling of the surface reaches saturation at about 1 μm and is due to voids in the substrate that are formed during the thermal spike phase of the collision cascade. A discolouring of the indium antimonide surface was also observed after implantation. The surface was black after P_4^+, As_4^+ and N_2^+ implantations and grey in other cases. The visual appearance did not change after the N^+ implantation. However, no explanation for the discolouring of the sample surface was offered.