

CHAPTER 8

SUMMARY OF RESULTS

Aluminium diffusion was investigated by NRA in five different semiconductors. Different experimental methods were employed. For in-diffusion investigation thin aluminium films were deposited onto the specimen followed by subsequent annealing. Aluminium diffusion within the investigated semiconductors was analysed after implantations at room temperature and $T_i = 250\text{ }^\circ\text{C}$ followed by subsequent annealing. The diffusion coefficients obtained were compared with previously reported results when available.

No aluminium in-diffusion was observed into any of the studied semiconductors. From this it can be concluded that within the respective temperature range aluminium is a suitable contact material for the investigated semiconductors.

From the diffusion enhancement of aluminium in the highly damaged elemental semiconductors silicon and germanium it can be concluded that the diffusion occurs via a vacancy mechanism in these materials as already suggested by *Seeger* et al. [8].

8.1. SILICON

The in-diffusion of aluminium into Si<100> at temperatures ranging from 500 °C to 900 °C has been investigated. Coefficients expected from previously published results are extrapolated to these temperatures. An extrapolation was necessary because most of the reported results were obtained for temperatures above 1000 °C. At 900 °C a diffusion coefficient between $D = 1.3 \times 10^{-13}\text{ cm}^2\text{ s}^{-1}$ and $D = 3 \times 10^{-15}\text{ cm}^2\text{ s}^{-1}$ with an average value of $D = 4 \times 10^{-14}\text{ cm}^2\text{ s}^{-1}$ is expected. Higher annealing temperatures in our vacuum system were avoided after complete oxidation of the thin aluminium film was observed during annealing at $T_a = 1000\text{ }^\circ\text{C}$.

No detectable aluminium in-diffusion was observed at any stage and an upper limit for the diffusion coefficient at $D \leq 10^{-16}\text{ cm}^2\text{ s}^{-1}$ was obtained for 900 °C, which is significantly

smaller than expected from the literature. However, a native layer of SiO_2 that forms instantaneously after cleaning the silicon surface before depositing the aluminium film acts as a diffusion barrier and thus reduces the diffusion during annealing. Therefore the actual diffusion coefficient is expected to be higher and could be in the interval calculated from the literature.

Aluminium diffusion within $\text{Si}\langle 100 \rangle$ and $\text{Si}\langle 111 \rangle$ was investigated after implantations at room temperature and at $T_i = 250 \text{ }^\circ\text{C}$ with subsequent annealing for one hour at temperatures up to $T_a = 900 \text{ }^\circ\text{C}$. By comparing aluminium depth profiles for room temperature implantation and for implantation at $T_i = 250 \text{ }^\circ\text{C}$, radiation enhanced diffusion for our implantation parameters has been calculated to be smaller than $D \leq 10^{-15} \text{ cm}^2 \text{ s}^{-1}$.

The room temperature implantation resulted in a highly disordered region that did only recover partly during annealing for one hour at $T_a = 900 \text{ }^\circ\text{C}$. An enhanced diffusion of the aluminium atoms to the surface was observed due to radiation induced damage. Complete aluminium out diffusion to the surface was observed at this temperature. The obtained diffusion coefficients at $900 \text{ }^\circ\text{C}$ are two to three orders of magnitude larger than those obtained for the implantation at $T_i = 250 \text{ }^\circ\text{C}$. However, they are in the same range as some of the published coefficients as seen in Fig. 28. We therefore believe that some of the higher results reported in the literature are due to defect enhanced diffusion. Our diffusion results after room temperature implantations are furthermore in accordance with the reported poor electrical activation due to out-diffusion and precipitation of Al_2O_3 at the surface after annealing at $T_a > 900 \text{ }^\circ\text{C}$ [63-69].

After implantation at $T_i = 250 \text{ }^\circ\text{C}$ radiation induced damage in the surface region was largely avoided and the aluminium-rich implantation region was bordered by a nearly defect-free surface region and the highly crystalline bulk. An upper limit for the diffusion coefficient at $D \leq 10^{-15} \text{ cm}^2 \text{ s}^{-1}$ was obtained for $900 \text{ }^\circ\text{C}$, which is significantly smaller than the smallest coefficients reported in the literature. It does not contradict our results obtained for in-diffusion.

During annealing the hot implanted silicon sample at $T_a = 900 \text{ }^\circ\text{C}$ two phases are expected in the implanted depth [55]. In a silicon depth of 200 nm we measured a maximum of about 5

at.% of aluminium. For this maximum density about 8 % of the compound is in the liquid phase, consisting of 37 % silicon and 63 % aluminium. The remaining 92 % in the solid phase consist mainly of silicon due to the low solubility of aluminium at this temperature. When cooling the sample down to room temperature aluminium segregates from the liquid [64].

8.2. GERMANIUM

The in-diffusion of aluminium into germanium at temperatures of 500 °C and 700 °C has been investigated. As expected diffusion coefficients from the literature are below our detection limit at 500 °C only the coefficients at 700 °C are extracted. No detectable diffusion is observed at any stage. From this we calculated an upper limit for the diffusion coefficient of $D \leq 10^{-16} \text{ cm}^2 \text{ s}^{-1}$ at 700 °C. This coefficient is about a magnitude lower than both previously reported coefficients $D = 1.2 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1}$ [71] and $D = 2.4 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1}$ [72]. These coefficients at 700 °C were measured by *Dorner* et al. [71], whereas the results by *Meer* et al. [72] were extrapolated from higher temperatures. Our upper limit for the diffusion coefficient is probably too low due to a thin native oxide layer that forms instantaneously after cleaning the germanium surface before depositing the aluminium film. This oxide layer forms a diffusion barrier and therefore lowers the extracted upper limit for the coefficient.

Aluminium diffusion within germanium was investigated after implantations at room temperature and to $T_i = 250 \text{ °C}$ with subsequent annealing for one hour at temperatures up to $T_a = 700 \text{ °C}$. From comparing the aluminium depth profiles after room temperature implantation with those after implantation at $T_i = 250 \text{ °C}$, an upper limit for the radiation enhanced diffusion was calculated at $D \leq 10^{-15} \text{ cm}^2 \text{ s}^{-1}$ for our implantation parameters, by taking into account the implantation time.

Channeling effects of α -particles were not observed in the implanted germanium samples due to a rather high dechanneling yield in the samples already before the implantation. However, when comparing the aluminium diffusion results in germanium with the results from the silicon investigation similarities are observed.

A comparison with the results obtained for the silicon implantation indicates that the room temperature implantation also resulted in an amorphous surface region that did only recover partly during annealing for one hour at $T_a = 500$ °C and $T_a = 700$ °C. Aluminium diffusion to the surface was observed after $T_a = 500$ °C due to radiation induced defects. Most aluminium atoms diffused out of the sample to the surface during $T_a = 700$ °C. The diffusion coefficient after room-temperature implantation is about two orders of magnitude larger than coefficients reported previously. However, the obtained diffusion coefficients are much too high due to the large amount of defects in the surface region and can therefore not be compared with coefficients expected in defect free germanium.

After implantation at $T_i = 250$ °C it appears from the similarity with the silicon results, that radiation induced damage in the surface region was largely avoided. However, a channeling effect was not observed. One reason for this is probably due to the fact that the mass of germanium is much larger than the mass of silicon, which leads to denser collision cascades and a dislocation network already at $T_i = 250$ °C.

An upper limit of the diffusion coefficient at $D \leq 10^{-15} \text{ cm}^2 \text{ s}^{-1}$ was obtained for 700 °C, which does not contradict the results by *Dorner* [71] and is slightly lower than the coefficient calculated from the results by *Meer* [72] (see Fig. 34).

From the binary phase diagram for the germanium aluminium system [70] it can be seen that at 700 °C two phases are formed in a germanium depth of 115 nm, where the aluminium reaches a maximum concentration of about 7 at.%. At this temperature about 17 % of the compound is in the liquid phase, consisting of 57 % germanium and 43 % aluminium. The solid phase consists mainly of germanium due to the low solubility of aluminium. When cooling the samples after annealing segregations of metallic aluminium are expected in the implanted depth.

8.3. GALLIUM ARSENIDE

The in-diffusion of aluminium into gallium arsenide at temperatures up to 500 °C was investigated. Expected diffusion coefficients at 500 °C are obtained when extrapolating the results from the literature in Fig. 18 to 773 K, which corresponds to a value on the abscissa of

1.3 and a diffusion coefficient of about $D \approx 10^{-30} \text{ cm}^2 \text{ s}^{-1}$. The expected coefficient is therefore much lower than our upper detection limit. However, radiation induced defects accounted for a dramatic diffusion enhancement in the elemental semiconductors investigated in this study. This investigation was made to analyse if defects also play such an important role in the aluminium diffusion in gallium arsenide.

As in the case for the other investigated semiconductors no detectable aluminium in-diffusion into gallium arsenide is observed at any stage. An upper limit for the diffusion coefficient of $D \leq 10^{-16} \text{ cm}^2 \text{ s}^{-1}$ is extracted for 500 °C, which is expected from the literature.

The aluminium diffusion within gallium arsenide was investigated after implantations at room temperature and at $T_i = 250 \text{ °C}$ with subsequent annealing for one hour at temperatures up to $T_a = 500 \text{ °C}$. When comparing the aluminium depth profiles after room temperature implantation and after implantation at $T_i = 250 \text{ °C}$ no difference could be detected. From this an upper limit of the radiation enhanced diffusion at $D \leq 10^{-15} \text{ cm}^2 \text{ s}^{-1}$ for our implantation parameters was extracted by taking into account the implantation time.

The room temperature implantation resulted in a highly disordered region. No channeling effect within the crystal was observed. No regrowth was observed after annealing at $T_a = 400 \text{ °C}$ for one hour. After annealing for one hour at $T_a = 500 \text{ °C}$ a channeling effect was observed in the crystal. However, the surface layer remained highly disordered. No aluminium diffusion through this highly disordered layer to the surface was observed. The upper limit of the aluminium diffusion coefficients for the room-temperature implantation is at $D \leq 10^{-15} \text{ cm}^2 \text{ s}^{-1}$ at 500 °C. For the elemental semiconductors a diffusion enhancement by a few orders of magnitude was observed. With an expected diffusion coefficient of about $D \approx 10^{-30} \text{ cm}^2 \text{ s}^{-1}$ defect enhanced diffusion by a few magnitudes could still take place without being detected by our method. The aluminium solubility in the investigated elemental semiconductors was very small which resulted in out diffusion from the room temperature implanted samples to the surface when annealing at elevated temperatures. When considering that the compounds AsAl and AsGa are completely miscible [105] and that the aluminium diffusion coefficient in gallium arsenide is strongly correlated to the gallium self-diffusion in this compound, then there is no aluminium out diffusion expected from the sample.

After implantation at $T_i = 250$ °C radiation induced disorder in the surface region was largely avoided as in the case of the elemental semiconductors. From the channeling spectra it is obvious that no amorphisation is present but the large slope of the dechanneling yield indicates a high density of extended defects.

A comparison of the aluminium depth profiles before and after annealing leads to the upper limit for the diffusion coefficient of $D \leq 10^{-15} \text{ cm}^2 \text{ s}^{-1}$ at 500 °C, which was expected.

8.4. INDIUM PHOSPHIDE

No previously reported results on the aluminium diffusion in indium phosphide were found in the literature. Predictions about the behaviour of this system are difficult for there are contradictory thermodynamic calculations of the aluminium solubility in this compound semiconductor [105]. Investigations in this study were performed up to 400 °C to avoid surface oxidation, which could influence the results.

Aluminium in-diffusion has been investigated at 400 °C by annealing thin aluminium films that were deposited onto clean indium phosphide substrates. The interface between the aluminium film and the indium phosphide substrate remained sharply defined after annealing. From this it was concluded that no detectable aluminium in-diffusion occurred at this temperature. An upper limit of the diffusion coefficient at $D \leq 10^{-16} \text{ cm}^2 \text{ s}^{-1}$ is extracted for 400 °C.

Aluminium diffusion within indium phosphide was investigated after implantations at room temperature and at $T_i = 250$ °C with subsequent annealing for one hour at temperatures up to $T_a = 400$ °C. The radiation enhanced diffusion for our implantation parameters, analysed by comparing the aluminium depth profiles for room temperature implantation and for implantation at $T_i = 250$ °C by taking into account the implantation time, was lower than our detection limit at $D \leq 10^{-15} \text{ cm}^2 \text{ s}^{-1}$.

The room temperature implantation resulted in a highly disordered surface layer that reached much deeper into the crystal than the mean ranges of the implanted aluminium ions. A slight crystalline regrowth from the bulk is observed after annealing the compound for one hour at

$T_a = 300$ °C. No further regrowth was observed from a sample that was subsequently annealed for one hour at $T_a = 400$ °C.

Müller et al. [106] measured thicknesses of amorphous surface layers in indium phosphide after 80 and 180 keV silicon room temperature implantation to be 150 and 290 nm, respectively. These results are more in line with the calculated damage thicknesses of 121 nm and 261 nm for these energies. However, their implantation parameters were rather different to ours, e.g. their dose rates were at 3×10^{11} ions $cm^{-2} s^{-1}$, which is more than thirty times lower and the fluences were at about 10^{14} ions cm^{-2} , which is about five hundred times lower than the parameters for this study. However, tail effects can be excluded as the reason for the observed enhancement in the damage depth when considering the measured aluminium depth profiles.

The aluminium depth profiles are unchanged before and after annealing for one hour at $T_a = 400$ °C. It was concluded that no detectable aluminium diffusion to the surface occurred. The diffusion coefficients in this case are also lower than our detection limit at $D \leq 10^{-15}$ $cm^2 s^{-1}$. We suspect a high aluminium solubility in indium phosphide after considering the aluminium out diffusion through highly damaged layers in elemental semiconductors where its solubility is low. The behaviour of this system is similar to the one observed for the Al-GaAs system, where the components were completely miscible in one other.

During implantation at $T_i = 250$ °C a different defect type is observed. The introduced damage reached about 1.5 times deeper than predicted from simulations and consists of a dense network of dislocations. No change in the dislocation density was observed during annealing for one hour at $T_a = 400$ °C.

The shape of the aluminium depth profile did not change before and after annealing for one hour at $T_a = 400$ °C. An upper limit for the diffusion coefficient at $D \leq 10^{-15}$ $cm^2 s^{-1}$ was extracted at 400 °C, which agrees well with the results obtained for the room temperature implantation and does not contradict the result obtained from the in-diffusion analysis.

8.5. INDIUM ANTIMONIDE

Previously reported results on aluminium diffusion in indium antimonide were not found. SbAl and InSb are miscible in all proportions to form (AlIn)Sb over most of the system [107]. From this fact very small diffusion coefficients are expected for this system.

For recording a NRA depth profile we had to implant high doses of at least 5×10^{16} aluminium ions cm^{-2} , to obtain a sufficient count rate in a reasonable analysing time. Longer analysing times bear the danger that target degradation occurs due to the analysing beam. Already relatively low ion fluences cause amorphisation of the indium antimonide target, where no α -particle channeling effect could be observed for the implanted samples.

Aluminium diffusion into indium antimonide was investigated after deposition of a thin aluminium film onto this compound followed by annealing at $T_a = 300$ °C. The interface between the aluminium film and the substrate remained unchanged before and after annealing. It was concluded that no detectable aluminium in-diffusion occurred at 300 °C. An upper limit for the aluminium diffusion coefficient at 300 °C is extracted to $D \leq 10^{-16} cm^2 s^{-1}$.

Aluminium diffusion within indium antimonide was investigated after implantations at room temperature and at $T_i = 250$ °C with subsequent annealing for one hour at a temperatures of $T_a = 300$ °C. A comparison of the aluminium depth profiles after room temperature implantation and after implantation at $T_i = 250$ °C revealed a dramatic difference. The depth profile after the hot implantation did not have a gaussian shape (Fig. 49), which was observed after the room-temperature implantation (Fig.48). Obviously aluminium atoms diffused out already during the hot implantation.

Annealing the room temperature implanted indium antimonide sample for one hour at $T_a = 300$ °C did not change the depth profile of the implanted aluminium. An enhanced aluminium diffusion to the surface due to radiation induced defects was not observed after annealing. Since no aluminium diffusion is detected an upper limit for the diffusion coefficients at 300 °C is $D \leq 10^{-15} cm^2 s^{-1}$.

A black discolouring of the sample surface was observed after the hot implantation, which is suspected to be the result of antimony loss from the surface during the implantation. Such an antimony loss leads to a phase transition with a liquid phase consisting mainly of indium (above 155 °C). When cooling down, an oxide layer (In_2O_3) can form on the surface [88]. Annealing a hot aluminium implanted indium antimonide sample for one hour at $T_a = 300$ °C results in aluminium out diffusion, which can also be explained with the antimony loss from the sample and the resulting vacancies that can enhance the diffusion.

8.6. OUTLOOK

The diffusion results in this study were obtained by NRA. A relatively high dose of aluminium has to be implanted to obtain depth profiles with a reasonable counting efficiency for a proton fluence that does not degrade the target surface. One possibility to increase the counting efficiency would be by replacing the intrinsic germanium detector with a second NaJ detector. This would enable our system to measure lower aluminium concentrations within a reasonable fluence of protons.

Another interest for future research lies in investigating the damage introduced into some of the semiconductors during hot implantation, which reveals a much deeper damage than expected from TRIM calculations. Damage ranges that are much deeper than the mean ranges of the implanted ions was previously only reported for metal targets [93], whereas in semiconductors the damage was usually found in the depth of the mean range [108]. A fluence and implantation temperature dependent investigation of this effect is intended.