Paper I

The effect of Si site-switching in GaAs on electrical properties and potential fluctuation

H. G. Svavarsson
J. T. Gudmundsson
G. I. Gudjonsson
H. P. Gislason

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The effect of Si site-switching in GaAs on electrical properties and potential fluctuation

H.G. Svavarsson, J.T. Gudmundsson, G.I. Gudjonsson, H.P. Gislason*

Science Institute, University of Iceland, Dunhaga 3, IS-107 Reykjavik, Iceland

Abstract

Si-doped GaAs layers were grown p-type at 700°C and n-type at 840°C by liquid phase epitaxy. Thermal annealing of the p-type samples at temperatures around 840°C converted the samples to n-type. We compare the as-grown and annealed samples by means of photoluminescence and temperature-dependent Hall and conductivity measurements. Highly doped samples converted to n-type through annealing become highly compensated. Their Hall mobility also increases more than an order of magnitude. Samples grown n-type at 840°C show up to three times higher mobility than the annealed ones. The compensation in each case was monitored through the shift of the photoluminescence bands with excitation intensity, up to 24 meV per decade of increase in the excitation power density for the highest compensation ratio. © 2001 Elsevier Science B.V. All rights reserved.

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Keywords: GaAs; Si-doping; Site-switching; Fluctuating potential

1. Introduction

At high growth temperatures, Si-doped GaAs samples grown by liquid-phase-epitaxy (LPE) are n-type but highly compensated, while at lower growth temperatures they are p-type [1–4]. The actual crossover-temperature depends on silicon concentration and crystal orientation [5]. Gallium arsenide grown by LPE from gallium melt is expected to be low in gallium vacancies and possibly high in arsenic vacancies [6]. Under these conditions, Si should predominantly be a shallow acceptor on As site. However, growth at high temperatures evidently favors Si on Ga sites. In the present investigation, we study the highly compensated regime of GaAs:Si and potential fluctuations resulting from insufficient screening of ionized impurities by free carriers [7]. In highly compensated semiconductors, the fixed charge may be randomly distributed and donor- and acceptor-rich regions may appear locally. Under normal circumstances, such fluctuations in the local potential are screened by mobile carriers, while the screening is insufficient in highly compensated samples. In photoluminescence (PL) measurements, potential fluctuations are manifested by a downward shift in photon energy of the near bandgap PL bands through localization of the charge carriers, as well as a shift of the localized PL bands to higher energy with increasing excitation power density. In GaAs, such fluctuations have been studied by photoluminescence in Li-compensated material [8] and highly Ge-doped material [9]. Here, we report on photoluminescence measurements of potential fluctuations in Si-doped GaAs, which has been converted from as-grown p-type to n-type by annealing above a certain transition temperature. Furthermore, we also correlate the defect density with the temperature-dependent Hall mobility of the majority carriers and compare the results from annealed samples with samples directly grown n-type.

*Corresponding author. Tel.: +354-525-4800; fax: +354-552-8911.

E-mail address: hafkid@hi.is (H.P. Gislason).

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2. Sample preparation and experiment

We grew about 1 μm thick GaAs films by liquid phase epitaxy on a semi-insulating GaAs (100) substrate. Four LPE batches were made. Keeping other growth conditions the same, the Si/Ga mass ratio in the growth solutions was altered from $(0.1–2.1)\times10^{-3}$ or $(0.3–5.2)\times10^{-3}$ mole fraction Si. Two GaAs samples were grown at 700°C, one with low Si concentration (sample #1), and another with higher Si concentration (sample #2). The other two LPE samples were grown at 840°C, one with low Si (sample #3) and the other with high Si (sample #4).

One piece of each sample #1 and #2 were baked in quartz ampoules at 840°C for 24 h with a subsequent quenching in liquid nitrogen. The sample derived from sample #1 was labeled #1a and similarly the one derived from sample #2 was labeled #2a. Table 1 summarizes the resulting data from the samples. To suppress arsenic vacancy V_{As} formation during baking, we placed a controlled amount of solid As into the ampoule prior to evacuation, giving an As gas pressure slightly below 1 bar at the baking temperature. Details of the sample preparation procedure are published elsewhere [10].

The free carrier concentration of the majority carriers and their Hall mobility were obtained by Hall measurements in the van der Pauw configuration. The Hall coefficient R_H was calculated from the slope of the Hall voltage versus the magnetic field in the range of 0–0.5 T, and an average of four values in each point was taken where the two pairs of contacts were interchanged and the current reversed. The conductivity was measured by the van der Pauw technique [11]. Then the Hall mobility is given by $\mu_H = R_H/\rho$, where ρ is the conductivity.

Photoluminescence measurements were performed at 14 K using the 532 nm line of a Verdi Nd:YVO4 laser from coherent as an excitation source. The excitation intensity was varied over several decades, from 0.001 to 0.1 W, and the laser beam was focused on an area of $\sim1\,mm^2$. For each series of excitation intensities the area was kept constant. The PL signal was detected via a double 0.85 m Spex 1404 grating monochromator using a cooled Ge detector.

3. Results and discussion

3.1. Annealing experiment

Both LPE samples grown at 700°C were p-type. Annealing of p-type samples around a crossover-temperature makes them highly compensated and eventually n-type at still higher temperatures. The compensation ratio is defined N_A^-/N_D^+ for n-type but N_D^+/N_A^- in the case of p-type material [12], where N_A^- is the concentration of ionized acceptors and N_D^+ that of ionized donors. This ratio can be varied with the annealing temperature. Annealing at 840°C converted samples #1 and #2 to n-type with rather similar electron concentration, sample #1a with $n = 3.9\times10^{17}\,cm^{-3}$ and sample #2a with $n = 1.9\times10^{17}\,cm^{-3}$. We note that in addition to the type conversion, there is a significant difference in the compensation ratio of sample #2 before and after annealing, since the net electron concentration in sample #2a is only about 10% of the original hole concentration. In the less Si-doped sample #1 the carrier concentration before and after annealing remains the same within a factor of two.

The type conversion from p- to n-type upon annealing may be caused by site-switching of silicon on arsenic site Si_{As} to form silicon on gallium site Si_{Ga} in As ambient gas according to the equation

$$\begin{gathered} Si_{As} + V_{Ga} \rightleftharpoons Si_{Ga} + V_{As} \\ \frac{As(g) + V_{As} \rightleftharpoons As_{As}}{As(g) + Si_{As} + V_{Ga} \rightleftharpoons Si_{Ga} + As_{As}} \end{gathered} \quad (1)$$

Driving the reaction to the right by increasing the ambient As gas pressure, either during growth or through annealing increases the concentration of Si_{Ga} according to Eq. (1).

3.2. Photoluminescence measurements

In the as-grown sample #1 with low Si concentration, the spectrum is dominated by a broad PL band peaking around 1.445 eV for the lowest excitation intensity level

Table 1
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

Low Si-doping level				High Si-doping level			
Sample	Carrier conc. (cm^{-3})	Shift (meV/dec.)	Mobility (cm^2/Vs)	Sample	Carrier conc. (cm^{-3})	Shift (meV/dec.)	Mobility (cm^2/Vs)
#1	$p = 1.6\times10^{17}$	6	110	#2	$p = 2.0\times10^{18}$	5	20
#1a	$n = 3.9\times10^{17}$	2.5	880	#2a	$n = 1.9\times10^{17}$	24	820
#3	$n = 1.4\times10^{16}$	8	2500	#4	$p = 3.9\times10^{17}$	8	50

used, I_{min} [10]. Increasing the excitation intensity shifts the peak position around 6 meV per decade of change, which we interpret as a shift caused by insufficient screening of ionized impurities. Annealing at 840°C dramatically changes the spectrum. The intensity becomes much smaller and a weak band at 1.385 eV at I_{min} shows a shift of 2–5 meV per decade of change in intensity.

The photoluminescence spectrum of the as-grown sample #2 with high Si concentration exhibits a broad, strong peak at 1.435 eV for an excitation level of I_{min}. This peak shows a rather similar shift with excitation intensity as found in sample #1. In this sample, the annealing produces a strong shift in the PL spectrum as illustrated in Fig. 1. A broad peak around 1.35 eV at I_{min} shifts some 24 meV per decade of change.

The shift rate of the two as-grown samples #3 (low Si concentration) and #4 (high Si concentration) is similar, close to 8 meV. Fig. 1 summarizes the dependence of the peak positions of the six as-grown and annealed samples on the excitation intensity. Table 1 also includes the observed shift rate of the PL bands. The localization caused by the potential fluctuation can be described as a lowering of the photon energy of PL transitions by twice the depth of a potential well [7]. In n-type semiconductors, this potential well depth is directly proportional to the ratio $N_t^{2/3}/n^{1/3}$ with p replacing n in p-type semiconductors. Here, N_t is the total concentration of charged impurities in the material which are assumed to have a Gaussian distribution. Hence, the well depth increases with increasing concentration of charged impurities, N_t, but decreases with increasing concentration of free charge carriers. Therefore, in the presence of potential fluctuations, one expects to find a shifting PL band at lowest photon energies in highly compensated semiconductors with a high original shallow doping. Also, one expects a shift to higher energies with increased excitation intensity which increases the concentration of photo-excited carriers. This is indeed what we observe.

Comparing the as-grown spectra of samples #1 and #2, we see that the shift rate with excitation intensity in Fig. 1, is comparable for both samples while the peak position is somewhat lower in energy for sample #2 which has a higher Si concentration. This is in general agreement with the higher concentration of ionized impurities, although the higher concentration of free carriers in sample #2 reduces the corresponding well depth.

The type conversion from p- to n-type through annealing illustrates a way of obtaining a striking range of compensation ratios. A significant difference between the two samples is evident upon annealing as shown in Fig. 1. The highly doped sample #2a shows a substantial shift, whereas the shift rate of the weakly doped sample remains low. Although the electron concentration of the two samples after annealing is rather similar, the large shift of the PL band in sample #2a is typical of a high concentration of compensated ionized impurities. The PL shift accompanies a reduction of the free carrier concentration by a factor of 10 in addition to the type conversion. The measured Hall concentration in the as-grown sample #2 can, therefore, be concluded to reflect the true Si_{As} concentration and a low compensation ratio, whereas the Si_{Ga} and Si_{As} concentrations become roughly similar upon annealing, with a compensation ratio approaching one as a consequence.

3.3. Electrical measurements

In Fig. 2, the Hall mobilities of the three samples with low Si-doping level, are compared. Sample #3 is n-type

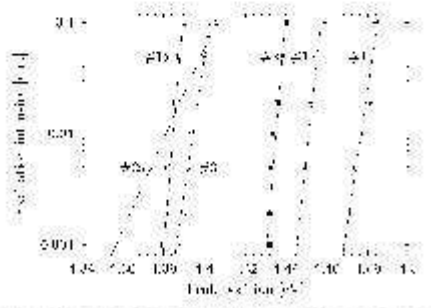

Fig. 1. PL peak position for different excitation intensity for the six samples. The slope of each curve represents the shift rate with excitation intensity.

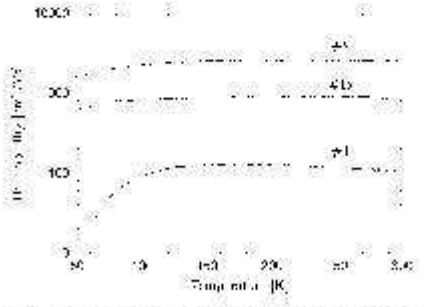

Fig. 2. The Hall mobility of low Si-doped GaAs as a function of temperature. Sample #1 is p-type GaAs, as-grown at 700°C; #1a is n-type GaAs, grown at 700°C and annealed at 840°C; #3 is n-type GaAs as-grown at 840°C.

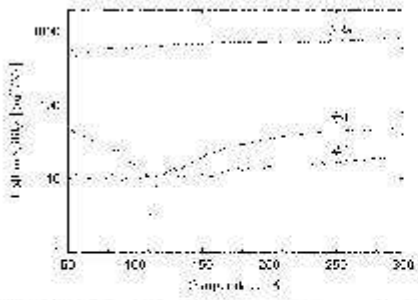

Fig. 3. The Hall mobility of high Si-doped GaAs as a function of temperature. Sample #2 is p-type GaAs, as-grown at 700°C; #2a is n-type GaAs, grown at 700°C and annealed at 840°C; #4 is GaAs as-grown at 840°C and is n-type below 105 K.

and has a Hall mobility of around 2500 cm^2/Vs at room temperature, whereas sample #1 grown at 700°C is p-type with a Hall mobility of 110 cm^2/Vs. After annealing at 840°C, the sample grown at 700°C has converted to n-type and its mobility increased nearly one order of magnitude, to 880 cm^2/Vs at room temperature (sample #1a).

Fig. 3 shows the Hall mobility data for samples grown and annealed at the same temperatures as in Fig. 2 but at ~20 times higher doping level. Here, the annealed sample #2a has the highest Hall mobility, 850 cm^2/Vs. Hall measurements show that the highly doped sample #4 exhibits p-type behavior at elevated temperatures but n-type behavior below 105 K. The minimum in the mobility curve for sample #4 is an artifact due to the Hall overshoot when $p = n(\mu_n/\mu_p)^2$ where the electrons and holes attempt to cancel the contributions of each other towards the Hall effect [13]. Here μ_n is the mobility of electrons and μ_p is the mobility of holes. Sample #3, grown at 840°C is n-type, whereas sample #4, grown at the same temperature but with much higher Si-concentration, is p-type above 105 K and n-type below. At this temperature the number of ionized donors and acceptors is equal.

Even though the mobility of samples #1 and #2 significantly increases upon annealing, it is still several times lower than that of sample #3. Most likely, the number of scattering centers has grown by the annealing. Presumably they include Ga vacancies and, to some extent, antisite defects.

4. Conclusion

Annealing at temperatures close to a transition temperature of 840°C resulted in closely compensated samples as verified by a shift of localized PL bands with excitation intensity. The presence of potential fluctuations is manifested through a shift of the PL peak position of up to 24 meV per decade of increase in the excitation power density. Furthermore, the annealing of p-type samples converted them into n-type with ~10 times higher mobility. We have correlated the observation of potential fluctuations with a possible site-switching of Si from As sites to Ga sites. Our results strongly suggest that the type conversion from p- to n-type may in fact be caused by such site-switching.

Acknowledgements

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Paper II

Potential fluctuations and site switching in Si-doped GaAs studied by photoluminescence

H. G. Svavarsson
J. T. Gudmundsson
G. I. Gudjonsson
H. P. Gislason

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Potential Fluctuations and Site Switching in Si-doped GaAs Studied by Photoluminescence

H. G. Svavarsson, J. T. Gudmundsson, G. I. Gudjonsson and H. P. Gislason

Science Institute, University of Iceland, Dunhaga 3, IS-107 Reykjavik, Iceland

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Abstract

We report on a photoluminescence (PL) study of highly compensated Si-doped GaAs. Si-doped GaAs layers were grown p-type at 700°C by liquid phase epitaxy and subsequently converted to n-type by thermal annealing at temperatures above a transition temperature of about 840°C. Annealing at temperatures close to the transition temperature resulted in a very high degree of compensation. This is verified by a large shift of photoluminescence bands with excitation intensity, up to 24 meV per decade of increase in the excitation power density. We attribute the shift to the presence of potential fluctuations which we correlate with a possible site-switching of Si from Ga sites to As sites. Our results strongly suggest that the type conversion from p- to n-type is in fact caused by site-switching of the Si impurity.

1. Introduction

The amphoteric nature of the Si impurity in GaAs is a well known fact. Substitutional group IV impurities in III-V semiconductors, such as Sn, Ge, or Si in GaAs, may occupy gallium sites where they behave as shallow donors, or arsenic sites where they are shallow acceptors. In particular, Si is known to behave amphoterically in GaAs [1]. For low total Si concentrations the solubility of Si donors occupying Ga lattice sites (Si_{Ga}) is greater than the solubility of Si acceptors occupying As lattice sites (Si_{As}). At very high Si concentrations a severe self compensation occurs [2]. When the total concentration of Si in GaAs exceeds 10^{18} cm^{-3} defect interactions become more complicated and we observe various kinds of interstitial or interstitial-substitutional complexes [3].

Ashwin *et al.* [4] and Spitzer *et al.* [5,6] found that at high growth temperatures Si-doped GaAs grown by liquid-phase-epitaxy (LPE) is n-type but highly compensated, while at lower growth temperatures it is compensated and p-type. The actual crossover point depends on temperature, silicon concentration and crystal orientation [7]. At low doping levels the carrier concentration tends to rise linearly with the total Si concentration $[Si]_{tot}$. Auto-compensation causes problem at high doping levels although carrier concentrations as high as $\sim 10^{20}$ cm^{-3} have been achieved by low temperature growth (300–600°C) [1].

A site-switching of silicon on arsenic site Si_{As} to form silicon on gallium site Si_{Ga} in As ambient gas may be formulated as follows:

$$\begin{aligned} &Si_{As} + V_{Ga} \rightleftharpoons Si_{Ga} + V_{As} \\ +\ &As(g) + V_{As} \rightleftharpoons As_{As} \\ \hline &As(g) + Si_{As} + V_{Ga} \rightleftharpoons Si_{Ga} + As_{As} \end{aligned} \qquad (1)$$

The Si_{Ga} is usually considered more mobile than Si_{As} [2] but at high temperatures (>840°C) the kinetics favor Si on Ga site. By looking at Eq. (1), one would except the reaction to be driven to the right by increasing the ambient As(g) pressure, thereby aiming for a higher concentration of Si on Ga sites, Si_{Ga}. Arsenic could also occupy the gallium vacancies but its affinity for arsenic vacancies is significantly higher. Gallium arsenide grown by LPE from gallium melt is expected to be low in gallium vacancy defects and possibly high in arsenic vacancies [8]. If GaAs is solution grown from gallium under conditions where there are few gallium vacancies, Si is a shallow acceptor.

The *degree* of compensation η is often defined as [9]

$$\eta = \frac{N_D^+ + N_A^-}{n} \qquad (2)$$

where n is the free electron concentration ($\simeq N_D^+ - N_A^-$) in n-type material. N_D^+ and N_A^- denote the concentration of ionized donors and acceptors, respectively. Similar equation is also valid for p-type material if n is replaced by $p = N_A^- - N_D^+$. An alternate approach is to define the compensation *ratio* as N_A^-/N_D^+ [9] for n-type but N_D^+/N_A^- in the case of p-type material.

By annealing p-type samples at temperatures around the transition temperature, they are converted to a highly compensated state and to n-type samples at still higher temperatures. Furthermore, the compensation degree can be varied with the annealing temperature, peaking to infinity at the transition temperature. In a review article by Newman [1] the lattice locations of silicon impurities in GaAs are summarized. Furthermore, they are related to the electrical properties of n-type Bridgman, liquid-encapsulated Czochralski (LEC), molecular beam epitaxial (MBE) (001) GaAs on the one hand, and to p-type liquid phase epitaxial and MBE (111) A layers on the other hand. Newman focused on highly doped n-type material and its saturation above 5×10^{18}–10^{19} cm^{-3}, depending on the type of GaAs material. In the present investigation we study the highly compensated regime of GaAs:Si and potential fluctuations caused by the reduction of Coulombic screening in the material.

Highly compensated semiconductors are known to exhibit potential fluctuations as a result of insufficient screening of ionized impurities by free carriers [10]. In photoluminescence (PL) measurements potential fluctuations are manifested by a downward shift in photon energy of the near bandgap PL bands through localization of the charge carriers, as well as a shift of the localized PL bands to higher energy with increasing excitation power density. This shift is much larger than that of donor-to-acceptor pair (DAP) bands with excitation intensity. Furthermore, in contrast to

ordinary DAP recombination, the bands shift to lower energy at higher temperatures.

In GaAs such fluctuations have been studied by photoluminescence in Li-compensated material [11] and in highly Ge-doped material [12]. Here we report on photoluminescence measurements of potential fluctuations in Si-doped GaAs, which has been converted from as-grown p-type to n-type by annealing above the transition temperature.

2. Sample preparation

A roughly 1 μm thick GaAs film was grown by liquid phase epitaxy on a semi-insulating (SI) GaAs (100) substrate. The substrate was brought into contact with liquid Ga metal of purity 6N at 700°C, saturated with As and containing dissolved Si. By lowering the temperature the solution becomes supersaturated with respect to As and the film growth nucleates at the substrate. The growth process took place in reducing H_2 ambient of purity 7N and in graphite crucibles. For this study two LPE batches were made, differing in the amount of Si in the growth solutions. While all other growth conditions were kept the same the Si/Ga mass ratio in the growth solutions was altered from 1.2×10^{-4} to 2.1×10^{-3} ($\simeq 3.0 \times 10^{-4}$ and 5.2×10^{-3} mole fraction, respectively). According to [8] this should correspond to a net hole concentration $\sim 3 \times 10^{17}$ and $\sim 5 \times 10^{8}\,\mathrm{cm}^{-3}$, respectively, in as-grown GaAs.

Si-doped GaAs grown by LPE is highly compensated for growth temperatures around 840°C. It is n-type and still quite compensated if grown at higher temperatures but p-type if grown at lower temperatures. Pieces of the two as-grown LPE batches were baked in quartz ampoules at 840°C for 24 h with a subsequent quenching in liquid nitrogen. To retard V_{As} formation during baking a small amount of As(s) was put into the ampoule prior to evacuation. The ampoules were closed at 1.0×10^{-5} mb pressure. Arsenic sublimates at 613°C. The amount of As in the ampoule was controlled to a given As(g) pressure slightly bellow 1 bar at the baking temperature.

3. Experiment

The free carrier concentration was obtained by Hall measurements. Using square samples, ohmic contacts were welded on the four corners with tin- or zinc-coated gold wire, tin in the case of n-type samples and zinc in the case of p-type samples. The ohmic contacts were made so to avoid heating while alloying the contacts. A typical sample size was $3 \times 3\,\mathrm{mm}^2$. The Hall coefficient R_H was estimated from the slope of the Hall voltage vs. the magnetic field in the range of 0–0.5 Tesla, Tesla, and an average of four values in each point was calculated where the two pairs of contacts were interchanged and the current reversed. Electron and hole concentrations were calculated from the Hall coefficient R_H as $n = -r_H/eR_H$ and $p = r_H/eR_H$, respectively, assuming the Hall scattering factor r_H to be isotropic, temperature independent and of unit value ($r_H \equiv 1$).

Photoluminescence measurements were performed at 14 K using a closed-cycle He cryostat. The 532 nm line of a Verdi Nd:YVO4 laser from Coherent was used as an excitation source. The excitation intensity was varied over several decades and the PL signal was detected via a double 0.85 m Spex 1404 grating monochromator using a cooled Ge detector. The spectra presented here were not corrected for the spectral response of the instruments. Hall measurements were performed to determine the majority carrier type. The nominator term in equation (2), $N_D^+ + N_A^-$, is assumed to be identical to the total concentration of silicon, $[\mathrm{Si}]_{tot}$ at room temperature whilst the denominator term is approximated by the free carrier concentration observed by the Hall measurements.

4. Experimental results

Two GaAs samples were grown p-type under the conditions described above. One was grown with a low Si concentration (Sample #1), $p = 1.6 \times 10^{17}\,\mathrm{cm}^{-3}$, and the other with a higher Si concentration (sample #2), $p = 4.0 \times 10^{18}\,\mathrm{cm}^{-3}$ Annealing converted both samples to n-type with rather similar electron concentration, sample #1a with $n = 3.9 \times 10^{17}\,\mathrm{cm}^{-3}$ and sample #2a with $n = 3.8 \times 10^{17}\,\mathrm{cm}^{-3}$. We note that in addition to the type conversion there is a significant difference in the compensation degree of sample #2 before and after annealing, since the net electron concentration in sample #2a is only about 10% of the original hole concentration. In the less Si-doped sample #1 the carrier concentration before and after annealing remains the same within a factor of two. Table I summarizes the carrier concentration of each sample.

As-grown, unintentionally doped GaAs exhibits bound exciton (BE) spectra around 1.51 eV and donor-acceptor (DAP) pair spectra which merge with free-to-bound (FB) around 1.49 eV when the donors become ionized. In lightly Si-doped samples the Si-donor to Si-acceptor pair band peaks at 1.482 eV at low temperatures, and the FB transition around 1.485 eV [13]. The band-edge PL bands are not observed on the intensity scale of Fig. 1(a), which shows the photoluminescence spectrum of the as-grown sample #1 with low Si concentration. Instead the spectrum is dominated by a broad PL band peaking around 1.445 eV at an excitation intensity level of 0.001 W.

The laser beam was focused to an area of $\sim 1\,\mathrm{mm}^2$. For each series of excitation intensities the area was kept constant. Increasing the excitation intensity of sample 1# by two orders of magnitude to 0.1 W shifts the peak position around 6 meV per decade of change in excitation intensity. In the discussion section we interpret this shift in terms of the presence of potential fluctuations caused by insufficient screening of ionized impurities. Annealing at 840°C dramatically changes the spectrum as shown in Fig. 1(b) (sample #1a). The intensity is much weaker as

Table I. *The carrier concentration in as grown and annealed samples obtained by Hall measurements and PL peak shift with excitation intensity in as grown and annealed samples measured at 14 K.*

Sample	Carrier concentration [cm^{-3}]	Shift [meV/decade]
#1	$p = 1.6 \times 10^{17}$	6 meV
#1a	$n = 3.9 \times 10^{17}$	5 meV
#2	$p = 4.0 \times 10^{18}$	5 meV
#2a	$n = 3.8 \times 10^{17}$	24 meV

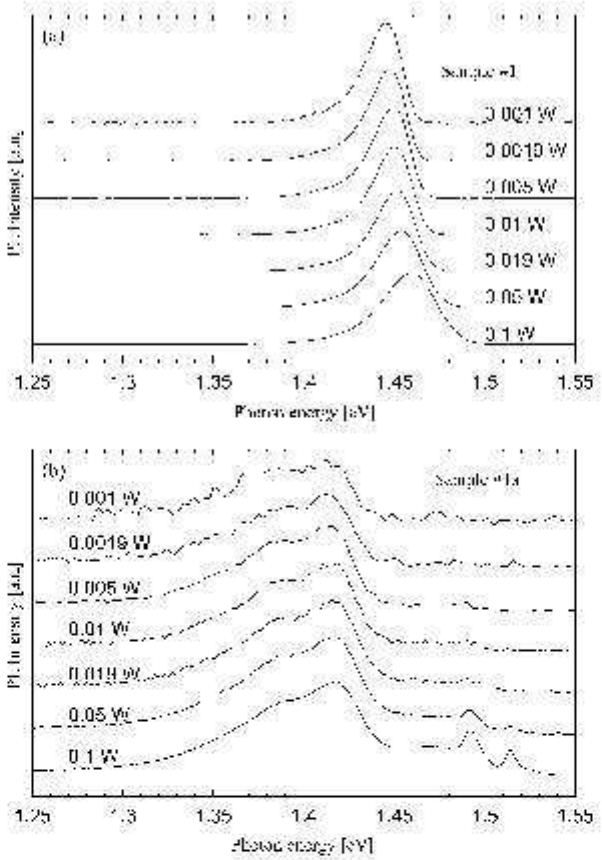

Fig. 1. Peak shift with excitation intensity of a PL band measured at 14 K in (a) as-grown p-type LPE sample grown to have low Si concentration and (b) the same sample n-type after annealing at 840°C for 24 h.

evidenced by the presence of the band-edge PL bands from unperturbed regions of the sample. These PL bands only shift insignificantly with excitation intensity, the DA pairs typically shifting less than 1 meV per decade. The main PL band peaking around 1.42 eV also shows a negligible shift with excitation intensity, thus originating from unperturbed regions of the sample. We attribute this band to defect-related transitions induced by the annealing. Another weaker band at 1.385 eV for the lowest excitation intensity shows a shift around 5 meV per decade of change in intensity. Hence, this band is an evidence for the presence of potential fluctuations after annealing.

Fig. 2(a) shows the photoluminescence spectrum of the as-grown sample #2 with high Si concentration. The spectrum exhibits a broad, strong peak at 1.435 eV for an excitation level of 0.001 W. This peak shows a similar shift with excitation intensity as sample #1, about 5 meV per decade of change. In this sample the annealing produces a strong shift in the PL spectrum as illustrated in Fig. 2(b). A broad peak around 1.35 eV at 0.001 W shifts some 24 meV per decade of change in excitation intensity. In addition, the spectrum shows the usual band-edge luminescence.

Figure 3 summarises the dependence of the peak positions of the as-grown and annealed samples on the excitation intensity. Table I lists the observed shift rate of the PL bands in addition to the carrier concentration of each sample.

5. Discussion

In highly compensated semiconductors the fixed charge may be randomly distributed. Donor- and acceptor-rich regions may appear locally and, hence, positively and negatively charged domains. Under normal circumstances such fluctuations in the local potential are screened by mobile carriers, while at high compensation degree the screening is insufficient. Radiative recombination in the depleted regions can be described as taking place between carriers confined to spatially separated potential wells which originate from fluctuations in the distribution of charged impurities [10,11].

The localization lowers the photon energy of donor-to-acceptor pair transitions by twice the potential well depth or

$$h\nu = E_g - (E_D + E_A) - 2\gamma(r_s) \qquad (3)$$

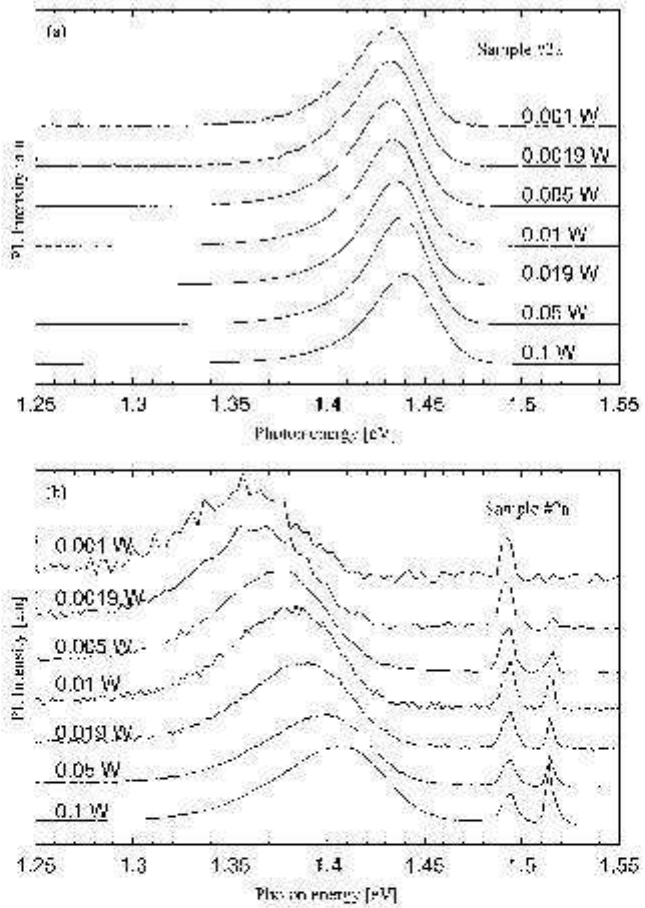

Fig. 2. Peak shift with excitation intensity of a PL band measured at 14 K in (a) an as-grown p-type LPE sample grown to have low Si concentration and (b) the same sample n-type after annealing at 840°C for 24 h.

where E_g is the band gap energy, E_D the ionization energy of the donor and E_A the ionization energy of the acceptor. The potential well depth is

$$\gamma(r_s) = \frac{e^2}{4\pi\varepsilon_0\varepsilon_s r_s}(N_i r_s^2)^{1/2} = \frac{e^2}{4\pi\varepsilon_0\varepsilon_s}\frac{N_i^{2/3}}{n^{1/3}} \tag{4}$$

where N_i the total concentration of charged impurities in the material and r_s is the screening radius defined as $r_s = N_i^{1/3}/n^{2/3}$ in the case of n-type semiconductors. The impurities are assumed to have Gaussian distribution.

From Eqs (3) and (4) we see that the well depth increases with increasing concentration of charged impurities N_i but decreases with increasing concentration of free charge carriers. From the equations one expects a PL band in the presence of potential fluctuations to shift to lowest photon energy in highly compensated semiconductors which originally had high shallow doping. Also one expects a shift to higher energies with increased excitation intensity which increases the concentration of photoexcited carriers. This is indeed what we observe.

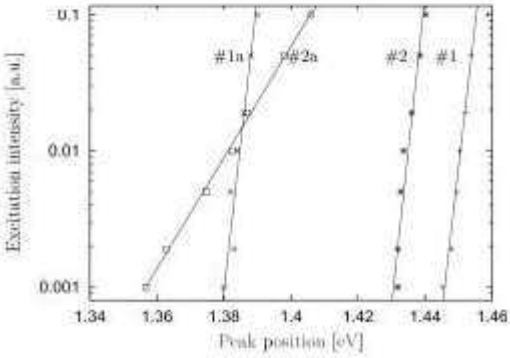

Fig. 3. PL peak position for different excitation intensities for the four samples. The slope of each curve represents the shift rate with excitation intensity.

In the present work we emphasize the two ways in which compensation can be obtained in Si-doped GaAs. The obvious one is direct growth under conditions which ensure close compensation of Si_{Ga} donors by Si_{As} acceptors. We have accomplished such doping as evidenced by the presence of shifting PL bands in the as-grown samples. Comparing the as-grown spectra of the two samples #1 and #2 in Fig. 3 we note that the shift rate with excitation intensity is comparable for both samples while the peak position is somewhat lower in energy for sample #2 which has a higher Si_{tot} concentration. This is in a general agreement with the higher concentration of ionized impurities according to Eq. (3), although the higher concentration of free carriers in sample #2 reduces the corresponding well depth.

The type conversion from p-type to n-type through annealing also illustrates a way of obtaining a striking range of compensation degree. A significant difference between the two samples is evident upon annealing as shown in Fig. 3. The highly doped sample #2a shows a substantial shift whereas the shift rate of the weakly doped sample remains low. Note that the PL and around 1.42eV in sample #1a in Fig. 1(a) is not a shifting PL band, while the shoulder on the high energy wing of that band indicates potential fluctuations. This difference can again be accounted for by Eq. (3). Although the electron concentration of the two samples after annealing is rather similar, the large shift of the PL band in sample #2a is typical of a strong concentration of highly compensated ionized impurities. The PL shift accompanies a reduction of the free carrier concentration by a factor of ten in addition to the type conversion. The measured Hall concentration in the as-grown sample #2 can therefore be concluded to reflect the lowest possible Si_{As} concentration and a low compensation degree η, whereas the Si_{Ga} and Si_{As} concentrations become roughly similar upon annealing, with a high compensation degree as a consequence. Due to the high As(g) concentration during annealing one might expect, to some extent, the formation of the deep donor As_{Ga} although we assume its concentration to be negligible compared to the measured carrier concentration.

6. Conclusion

Annealing at temperatures close to a transition temperature of 840°C resulted in a very high compensation ratio as verified by a large shift of localized PL bands with excitation intensity. The presence of potential fluctuations is manifested through a shift of the PL peak position of up 24meV per decade of increase in the excitation power density. We have correlated the observation of potential fluctuations with a possible site-switching of Si from Ga sites to As sites. Our results strongly suggest that the type conversion from p- to n-type to is in fact caused by such site switching.

Acknowledgements

This work was partially supported by the Icelandic Research Council and The University of Iceland Research Fund.

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Paper III

Lithium induced vacancy formation and its effect on the diffusivity of Lithium in Gallium Arsenide,

H. P. Gislason
K. Leosson
H. Svavarsson
K. Saarinen
A. Mari

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LITHIUM INDUCED VACANCY FORMATION AND ITS EFFECT ON THE DIFFUSIVITY OF LITHIUM IN GALLIUM ARSENIDE

H.P. Gislason, K. Leosson, H. Svavarsson, K. Saarinen[1] and A. Mari[2]
Science Institute, University of Iceland, Dunhaga 3, 107 Reykjavik, Iceland
[1]Laboratory of Physics, Helsinki University of Technology,
P.O. Box 1100, FIN-02015 HUT, Finland
[2]Laboratoire d'Optique des Solides, Case 80, Université Pierre et Marie Curie,
4, Place Jussieu, F-75252 Paris cedex 05, France

Keywords: GaAs, vacancies, antisites, lithium, positron annihilation, diffusivity, local modes

Abstract. Diffusivity studies on Li in GaAs, where high concentrations of lithium have been introduced into undoped n-type starting material, reveal that diffusion of Li is trap-limited due to formation of complexes containing Li and native defects. The same defect complexes are found in Li-doped semi-insulating starting material and in p-type GaAs:Zn as well after passivation of the Zn acceptors. In partially Li-passivated Zn-doped starting material the Li is found predominantly in Li-Zn complexes which have a relatively low binding energy. In this case, the trapping effect is weak and the lithium exhibits high diffusivity. Using infrared absorption and positron lifetime measurements we investigate complexes of Li atoms and native defects which are formed in the Li-diffusion process. We observe significant V_{Ga} and Ga_{As} concentrations in the samples and demonstrate enhanced concentration of these native defects upon heat treatment. We show that Li also forms complexes with these native defects at low diffusion temperatures.

Introduction

Lithium, like hydrogen, exhibits a strong tendency to form complexes with other impurities and native defects when migrating in crystals. In such cases, the diffusion kinetics are largely affected by the binding energy of the complexes in question. A 1.0-eV activation energy for diffusion of Li in GaAs, sometimes cited as intrinsic in the literature, e.g. [1, 2], was determined by Fuller and Wolfstirn [3] near the solubility limit of Li in GaAs, $[Li] \approx 10^{19}$ cm^{-3}. This value is evidently too high to represent the intrinsic diffusivity; lithium is found to diffuse readily even below room temperature and recent measurements yielded a 0.85 eV dissociation energy of Li-Zn complexes [4], defining an upper limit for the intrinsic migration energy of Li.

Fuller and Wolfstirn [3, 5] investigated in-diffusion of Li to the saturation limit in GaAs at 800 °C and a subsequent out-diffusion by heat treatment. Starting materials were undoped n-type GaAs, S-doped ($\approx 10^{17}$ cm^{-3}) and Te-doped ($\approx 10^{18}$ cm^{-3}) GaAs. The authors suggested that Li was introduced as $Li_i^+ Li_{Ga}^-$ pairs during diffusion. While this simple model has not been verified by localised-vibrational-mode (LVM) experiments, Levy and Spitzer [6] reported LVM bands originating from five different Li-complexes, a donor, an acceptor and up to three neutral complexes in originally undoped GaAs after Li diffusion at high temperatures. All of these were attributed to two or more Li atoms associated with native defects of unknown origin.

This paper presents results of low-temperature reverse-bias and zero-bias annealing experiments on Li-rich undoped GaAs starting material and highly Li-doped p-type GaAs. Charge density profiles are monitored during reverse-bias annealing, yielding dissociation energies of defect complexes. Similar measurements during zero-bias annealing give information about the activation energies for trap-limited diffusion in the different materials. In p-type GaAs:Zn with low Li concentration, the pairing interaction is weak enough to allow determination of the intrinsic diffusivity. Conversely, in the Li-rich samples we find that the lithium diffusion is strongly trap limited. LVM measurements indicate that the migration is governed by pairing interactions with native defects. Positron annihilation experiments, performed in order to identify these defects, reveal significantly enhanced V_{Ga} and Ga_{As} concentrations both in as-diffused samples and after heat treatment.

Experimental

All starting materials were grown by the horizontal Bridgman method. For electrical measurements, nominally undoped GaAs ($n_{RT} = 1 \times 10^{16}$ cm^{-3}) and Zn-doped GaAs ($p_{RT} = 4 \times 10^{19}$ cm^{-3}) were used. Fourier transform infrared (FTIR) absorption measurements were carried out on several starting materials ranging from heavily Zn-doped p-type to nominally undoped n-type and semi-insulating starting

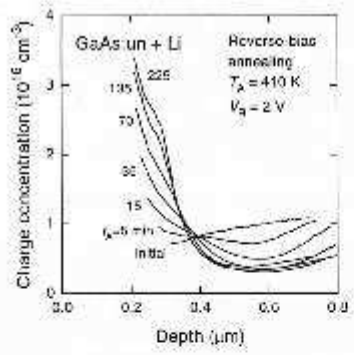

Fig. 1. Charge density profiles in Li-rich undoped GaAs during reverse bias annealing at 410 K. Measurements were performed at 270 K after rapid cooling of the sample.

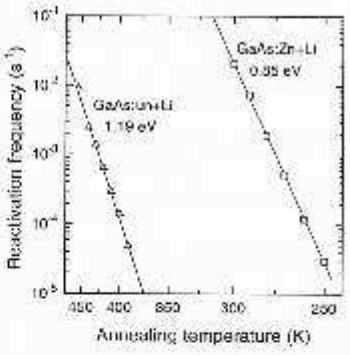

Fig. 2. Arrhenius plots of reactivation frequencies in Li rich undoped GaAs and lightly Li-doped p-type GaAs:Zn materials. Activation energies are indicated in the figure.

materials. Li diffusions were made using open-tube diffusions as described elsewhere [7]. Schottky diodes were formed on p-type material by evaporating 1000 Å thick aluminium dots of diameter 1 mm on the sample surface. Gold dots of similar dimensions gave Schottky diodes on n-type material. Ohmic contacts were made by welding Zn- or Sn-coated gold wire to the surface of p- and n-type samples, respectively. Annealing experiments were carried out in vacuum using a Joule-Thompson refrigeration system. C(V) profiles were measured using a 1 MHz Boonton 72B differential capacitance meter. FTIR measurements were performed using DA3+ and DA8 Bomem interferometers equipped with a globar light source and mylar-Si beam splitters. The transmitted light was detected with a bolometer. Samples were cooled in a continuous flow cryostat at 6 K. Positron lifetime measurements were performed and analysed at Helsinki University of Technology, as described in Ref. 8.

Reverse-bias annealing

Reverse-bias annealing of Schottky diodes was carried out using the method of Zundel and Weber [9]. Samples from nominally undoped starting material which remained n-type after Li diffusion exhibited high thermal stability, and the charge density profiles were unchanged after reverse-bias annealing at temperatures up to 200 °C. We conclude that the compensating Li acceptor resides in stable configurations, either substituting for Ga or forming acceptor complexes of Li_{Ga}, Li_i and native defects. In p-type starting material containing Li, however, significant charge transfer is observed after annealing under bias. This behaviour has been attributed to electric-field drift of Li^+ [4].

Figure 1 shows charge concentration profiles measured in undoped GaAs starting material, converted to p-type by Li-diffusion at 500 °C for 20 hours. The Hall hole concentration at room temperature was 2×10^{15} cm^{-3} and the Li concentration deduced from SIMS measurements of similar samples was around 10^{17} cm^{-3} [10]. Profiles were recorded after successive reverse-bias conditions followed by rapid cooling down to the measurement temperature. Annealing temperatures were in the range 390–455 K. After zero-bias annealing at 460 K for 30 minutes initial conditions were restored in the sample. The reactivation frequencies which describe the thermal dissociation of the passivated negative centres [9] are given in the Arrhenius plot in Fig. 2, from which the dissociation energy $E_a = 1.19 \pm 0.03$ eV is deduced. Also shown are the reactivation frequencies measured in Li passivated GaAs:Zn which give the much lower dissociation energy $E_a = 0.85 - 0.02$ eV, attributed to the dissociation of Li-Zn complexes [4].

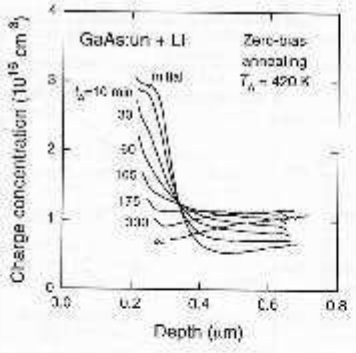

Fig. 3. Charge concentration profiles in Li-rich undoped GaAs material during zero-bias annealing. Initial curve was created under 2-V reverse bias at 420 K for 3 hours. Profiles were measured at 270 K after rapid cooling of the sample.

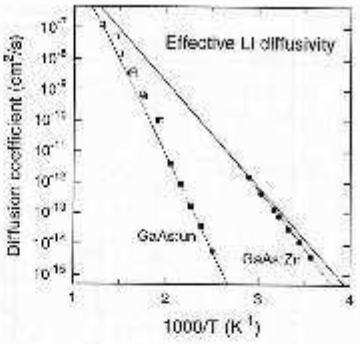

Fig. 4. Arrhenius plots showing effective diffusion coefficients of Li in Li-rich undoped GaAs and lightly Li-doped Zn-doped starting material. The solid line represents a calculation of the intrinsic diffusivity in the latter. Open squares are taken from Ref. 3. Dotted lines represent effective diffusivity [12].

Zero-bias annealing

The charge density profile was monitored during zero-bias annealing at different temperatures. Figure 3 shows the restoration of the equilibrium profile after a step had been created in the charge density profile with prolonged reverse-bias annealing. The step disappears after several hours at 420 K as shown in the figure. The effective diffusivity of Li is determined from the zero-bias profiles as described in detail elsewhere [11]. Diffusion coefficients are shown on an Arrhenius plot in Fig. 4. Results of the high-temperature diffusion experiments of Fuller and Wolfstirn [3] are included in the figure. The activation energy for diffusion determined for the Li-rich undoped starting material is 1.20 ± 0.03 eV. This value agrees with the complex dissociation energy derived from the reverse-bias annealing, indicating that in this material the diffusion behaviour is independent of the intrinsic diffusivity of Li and is governed by defect interactions. We note that the high-temperature diffusion data of Fuller and Wolfstirn agree fairly well with our measurements in strongly Li-doped samples. Exact agreement is not expected since the trapping process is predicted to depend on the concentration of Li and native defects in the material.

There is a frequently expressed concern that the strong electric field present in the depletion region of a junction affects the dissociation energy deduced from reverse-bias measurements. Dissociation energies determined from our reverse-bias and zero-bias annealing data agree to within error, and no significant high-field lowering of the complex dissociation energy takes place. It should be noted, however, that particularly low values of reverse bias, 1.5-2.0 V, were used in this work.

The intrinsic diffusion coefficient

In the case of partially passivated Zn-doped starting material, an activation energy of 0.75 ± 0.02 eV was determined from the diffusivity data of Fig. 4. This value deviates from the 0.85 eV dissociation energy measured in the Li-passivated GaAs:Zn, indicating that the diffusivity is not controlled exclusively by complex formation and dissociation. Given this and using the expression for the effective diffusivity from Zundel and Weber [12] we can calculate the intrinsic diffusivity D_i. The calculation yields $D_i = D_o \exp(-E_m/kT)$ with $E_m = 0.67 \pm 0.02$ eV, as illustrated by the solid line in Fig. 4 [11]. For details of the analysis see Leosson and Gíslason [11]. In the Li-rich material it is clear from Fig. 4 that the impurity migration is controlled by the 1.20 eV complex dissociation energy. Using the effective diffusivity in the strong trapping limit, one obtains a good fit to the experimental data by assuming a concentration of trapping centres around 4×10^{19} cm^{-3}. In this limit, the effective

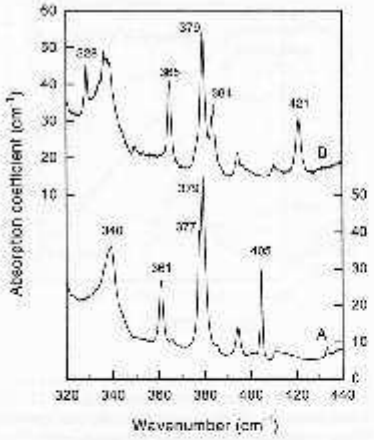

Fig. 5. FTIR absorption spectra of localised modes in GaAs. Curve A was measured in Li-diffused Zn-doped GaAs, but curve B in Li-diffused, undoped s.i. material.

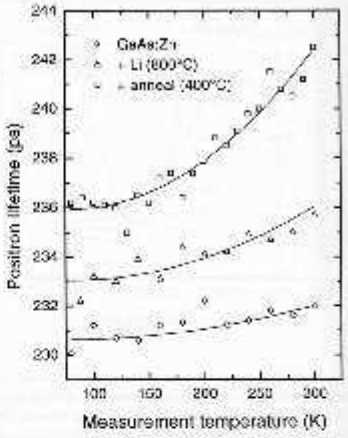

Fig. 6. Temperature variation of the positron lifetime in a GaAs:Zn reference sample, the same material after Li-diffusion at 800 °C and finally after a subsequent heating.

diffusivity is independent of D_i as pointed out above and no information about the intrinsic diffusivity in this temperature range can be obtained from the experimental data.

Native defects in strongly doped GaAs:Li

We now focus on the nature of the defects which are created by the diffusion of lithium into undoped, n-type, p-type and semi-insulating GaAs starting material. Curve A of Fig. 5 shows the Li-related LVM spectrum of GaAs:Zn co-doped with Li at 850 °C which gives a lithium concentration similar to the concentration of the Zn acceptor ($p = 1.4 \times 10^{19}$ cm^{-3}). Under these conditions, the p-type samples are highly resistive through passivation of the Zn acceptors by Li [10]. The vibrational modes at 340, 361, 377 and 405 cm^{-1} are attributed to neutral complexes of Li and Zn [10, 13]. As long as the Zn concentration exceeds that of Li, only these four peaks are present. Higher Li concentration makes the four Li-Zn peaks gradually disappear while five new LVM peaks appear, at 328, 365, 379, 384 and 421 cm^{-1}. This LVM spectrum was previously observed by Levy and Spitzer [6] in originally undoped GaAs although relative peak intensities vary between samples. Weaker peaks appear as well but will be ignored here. Note that the 379 cm^{-1} peak is already present in curve A, while the others are absent. In early work [6] the 379 cm^{-1} peak (being strongest in p-type starting material) was assigned to a Li related donor complex. The same five peaks also appear after Li diffusion of n-type and semi-insulating starting materials. Curve B of Fig. 5 shows this spectrum in a semi-insulating starting material after Li-diffusion at 850 °C. On account of its relative strength in n-type starting material the 365 cm^{-1} peak was attributed to an acceptor complex involving Li. The three remaining peaks were attributed to neutral defect complexes.

Heavy lithium doping of all GaAs starting materials makes the samples semi-insulating with a strong Li related localised vibrational mode spectrum resembling curve B. The Hall mobility of free carriers always decreases in samples with the appearance of the five Li-related localised vibrational modes. Evidently, self-compensating Li-related donor and acceptor complexes are formed at high lithium doping levels, in agreement with the LVM results. These impurities act as effective scattering centres for the charge carriers when ionised, thereby reducing the free carrier mobility. Mixed isotope doping experiments suggest that all of the five above complexes, responsible for the Li-related absorption peaks in curve B, involve two or more Li atoms in addition to native defects of unknown origin [6].

Table 1. Concentration of Ga vacancies and Ga antisite defects in different types of GaAs starting materials as determined by positron annihilation measurements.

Sample/ treatment	*Li conc. [cm^{-3}]*	*Carrier conc. [cm^{-3}]*	*Vacancy conc. [cm^{-3}]*	*Negative ion conc. [cm^{-3}]*
A. High doping level				
GaAs:Zn reference	none	p = 1 x 10^{19}	< 1 x 10^{15}	not detectable
Li: 800 °C	≈ 10^{19}	highly resistive	3.0 x 10^{16}	3.7 x 10^{17}
annealed 400 °C	≈ 10^{19}	p-type conducting	1.3 x 10^{17}	6.5 x 10^{17}
GaAs:Si	none	n = 2 x 10^{18}	< 2 x 10^{16}	< 2 x 10^{17}
Li: 800 °C	≈ 10^{19}	highly resistive	2.4 x 10^{16}	1.4 x 10^{17}
annealed 400 °C	≈ 10^{19}	p-type conducting	1.0 x 10^{17}	3.5 x 10^{17}
GaAs: undoped	none	semi-insulating	1.4 x 10^{16}	7.0 x 10^{15}
Li: 800 °C	≈ 10^{19}	highly resistive	1.4 x 10^{16}	7.0 x 10^{15}
annealed 400 °C	≈ 10^{19}	p-type conducting	2.2 x 10^{16}	1.0 x 10^{17}
B. Low doping level				
1 GaAs undoped	none	semi-insulating	1.2 x 10^{15}	5.0 x 10^{16}
2 Li 400 °C	2 x 10^{17}	semi-insulating	1.2 x 10^{15}	5.0 x 10^{16}
3 Li 400 °C/40 h	5 x 10^{17}	highly resistive	2.6 x 10^{16}	1.0 x 10^{17}
4 Li 500 °C/20 h	5 x 10^{17}	p = 1 x 10^{16}	0.8 x 10^{16}	2.5 x 10^{16}
5 #4 ann. 400 °C	2 x 10^{16}	p = 2 x 10^{16}	4.2 x 10^{16}	4.5 x 10^{17}

In order to identify the native defects in strongly Li-doped and heat-treated GaAs we performed positron lifetime measurements on different kinds of Li-diffused starting materials. We investigated strongly Li doped samples from n-type GaAs:Si, p-type GaAs:Zn and undoped semi-insulating GaAs starting materials on the one hand. On the other hand, we measured weakly Li doped semi-insulating starting material. Figure 6 shows the temperature variation of the positron lifetime in GaAs:Zn starting material, GaAs:Zn Li-diffused at 800 °C, and finally the latter sample annealed in As-saturated Ga melt at 400 °C. The latter two are typical of increased negative vacancy concentration since the average positron lifetime is longer than the one in as-grown samples. However, the decreased lifetime at low temperatures is indicative of negative ions which bind the positrons at temperatures below 150 K corresponding to a binding energy around 50 meV. Table I summarises the analysis of the positron lifetime measurements interpreted in terms of a defect containing a monovacancy and a negative ion containing no open volume. We suggest that the former is the V_{Ga} acceptor or an acceptor complex including a Ga vacancy and the latter the double Ga_{As} acceptor. The V_{Ga} acceptor complex may include the Ga_{As} acceptor, while the defect acting as a negative ion does not include vacancies. From the table we conclude that Li doping at 800 °C acts to increase the concentration of both V_{Ga} and Ga_{As}. It is obvious, however, that the Li concentration is not directly correlated to that of native defects. Instead the removal of lithium from the bulk enhances the latter. This is evident for all three starting materials in Table IA. Fuller and Wolfstirn observed that all Li-doped originally n-type samples showed p-type conductivity after heat treatment which removed the lithium [3, 5]. The undoped starting material exhibited 10^{17} cm^{-3} < p < 10^{18} cm^{-3}, while the n-type starting materials showed similar values, which corresponds to a higher acceptor concentration. The acceptors were found to be readily removed from the undoped samples at 800 °C and suggested to be Ga vacancies. Similarly, we observe strongly enhanced p-type conductivity in all Li-diffused starting materials after heat treatment at 400 °C, with hole concentrations up to 10^{19} cm^{-3}. In p-type starting materials, in particular, the final hole concentration is not related to or limited by the original shallow doping.

Native defects in weakly doped GaAs:Li

Photoluminescence (PL) bands at 1.34 and 1.45 eV are observed after Li diffusion of n-type GaAs between 400 and 600 °C [14]. Both bands are present in Li-doped semi-insulating starting materials as well but the 1.34 eV band is usually weak. In an earlier communication [15] we reported sharp PL lines at 1.508 and 1.510 eV which appear in semi-insulating GaAs starting material at low lithium

Table II. Concentration of V_{Ga} and Ga_{As} in Li-doped semi-insulating GaAs listed in order of intensity of bound exciton lines at 1.508 and 1.510 eV relative to other spectral features in the samples.

		Intensity of 1.508 and 1.510 eV bound exciton lines →				
Sample number		#1	#4	#2	#3	#5
BE line intensity		no lines	no lines	weak	strong	very strong
Li concentration	[cm^{-3}]	none	5.0×10^{15}	2.0×10^{15}	5.0×10^{15}	2.0×10^{16}
V_{Ga} concentration	[cm^{-3}]	1.2×10^{15}	0.8×10^{15}	1.2×10^{16}	2.2×10^{16}	4.2×10^{16}
Ga_{As} concentration	[cm^{-3}]	5.0×10^{15}	2.5×10^{15}	5.0×10^{15}	1.0×10^{17}	4.5×10^{17}

doping levels. The lithium diffusions were made at temperatures between 350 and 500 °C for periods of time ranging from a few hours to 40 h. The bound exciton lines were found to disappear for high lithium concentrations in the samples. PL bands with energies 1.34 and 1.45 eV have also been observed by Yu et al. after heat treatment of n-type samples at a much higher temperature than the Li diffusions, or 950 °C [16]. These authors assigned both PL bands to the two levels of an intrinsic V_{As}-Ga_{As} double acceptor. This heat treatment also gave rise to a pair of sharp lines at 1.508 and 1.510 eV which the authors associated with the same acceptor levels [16]. It was concluded in Ref. 15 that the two pairs of bound exciton lines were identical. However, it was pointed out that the lines appear in lithium-diffused samples at much lower temperatures than after annealing in vacuum [16]. Also, the relative intensity of the BE lines is greater in Li-doped samples. Table IB summarises the results of positron lifetime measurements for the semi-insulating starting materials after Li-diffusion at moderate temperatures while Table II presents the same results in order of increasing intensity of the BE lines.

The bound-exciton line intensity is found to be correlated to the concentration of V_{Ga} and Ga_{As} but independent of the Li concentration. This is particularly obvious for samples #4 and #5. Figure 7, curve A, shows the PL spectrum of sample #4 (made from a semi-insulating starting material by Li-diffusion at 500 °C for 20 h) in which no bound exciton lines can be detected at 1.508 and 1.510 eV. Annealing of sample #4 at 400 °C for 2 hours, however, gives rise to strong BE lines as shown for sample #5 in Fig. 7, curve B. The annealing strongly increases the concentration of V_{Ga} and in particular Ga_{As} while the Li concentration decreases as listed in Table II.

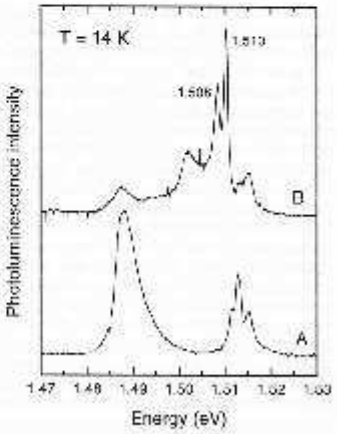

Fig. 7. PL spectra of semi-insulating GaAs starting material, Li diffused at 500 °C, before (curve A) and after (curve B) heat treatment at 400 °C. BE lines at 1.508 eV and 1.510 eV appear after the latter.

Model for the vacancy formation

Growth of GaAs under Ga-rich conditions is known to enhance the formation of arsenic vacancies, V_{As}. In samples containing a high concentration of V_{Ga} the V_{Ga}-Ga_{As} pair is likely to be created by a single gallium atom hop into the arsenic vacancy, $V_{As} \rightarrow V_{Ga} + Ga_{As}$. Theoretical calculations by Baraff and Schlüter [17] suggest that its formation energy is positive in p-type crystals but negative in n-type crystals. Moreover, the binding energy of the V_{Ga}-Ga_{As} pair is lower in n-type crystals than p-type [17]. Hence, the Ga_{As} antisite is expected to dominate over the V_{Ga} in Ga-rich ambience, at least when the Fermi level is mid-gap or higher. In p-type crystals, on the other hand, one might expect the V_{As}-Ga_{As} pair to be stable. Significant concentrations of V_{Ga} and Ga_{As} are present in the samples after Li diffusion at 800 °C into different kinds of starting material and subsequent heat treatment at 400 °C.

From Table I we note that Ga_{As} is favoured in all of the starting materials under these conditions. The strongest Ga_{As} concentration is found in the p-type GaAs:Zn starting material, which might seem to contradict the above considerations. However, LVM measurements show that complexes of Li and native defects are not formed until full passivation of acceptors has taken place for Zn concentrations as high as 10^{19} cm^{-3}. Although the passivated complexes are not stable at 800 °C the material is semi-insulating by means of charge compensation when the Li diffusion promotes the formation of Ga_{As}. The V_{Ga} concentration is enhanced as well, in fact it always seems to follow the Ga_{As} concentration at a level around a decade lower. This type of correlation is not an artefact of the analysis, since it is not generally observed [8]. The above analogy with Ga-rich growth conditions is brought about by the fact that our Li diffusion is performed in a Ga melt, thus resembling LPE conditions. However, at the low and intermediate diffusion temperatures employed, the high activation energy for Ga self-diffusion in GaAs severely limits the concentration of Ga_i in the bulk. Instead, we propose the following sequence of events to explain our observations. The presence of Li in the Ga melt in the diffusion process ensures a large concentration of rapidly migrating positively charged Li_i^+ donors in the GaAs bulk. It is well known that the formation energy of oppositely charged pairs is lower than that of isolated charged species, see e.g. [17]. In view of the well known tendency of Li^+ to passivate acceptors in GaAs we suggest that the formation of passive complexes involving interstitial Li donors and V_{Ga} acceptors as well as Li donors and Ga_{As} acceptors is energetically favourable. We hesitate to postulate a similar enhancement of V_{As} donors through interaction with negative interstitial Li acceptors if they exist, since we have never observed signs of negatively charged mobile Li ions. However, the participation of the substitutional Li_{Ga} acceptor in the above complexes is by no means excluded. In fact, we suggest that combinations of V_{Ga}, Ga_{As}, Li_{Ga} and Li_i and perhaps other defects account for the five complexes of Li and native defects which give rise to the LVM spectra of curve B in Fig. 5.

Annealing at 400 °C releases the lithium from the defect complexes, leaving V_{Ga} and Ga_{As} in abundance in the lattice, isolated or as complex defects. These defects are detected in our positron measurements as enhanced negative vacancy and negative ion concentrations. The fact that we always observe a much lower V_{Ga} concentration than Ga_{As} concentration may be caused by the Ga vacancy being more unstable than the Ga antisite, as described by the reaction $V_{Ga} \rightarrow As_{Ga} + V_{As}$ [17]. The presence of Li during heat treatment may be claimed to enhance the V_{Ga} and Ga_{As} concentrations from two points of view. First, heat treatment alone at 400 °C would not produce these defects. Second, heat treatment at 800 °C under Ga-rich conditions should, if anything, reduce the vacancy concentration. Therefore it is the presence of the ionised interstitial Li donors strongly interacting with the negatively charged V_{Ga} and Ga_{As} acceptors which stabilises these acceptors. We point out that reference samples annealed in Li-free Ga melt at 800 °C do not exhibit increased hole conductivity. For example, annealing of the semi insulating starting material of Table IA neither produces p-type conductivity nor any signs of the LVM spectrum in curve B of Fig. 5. Most samples show increased vacancy and antisite concentrations already after the Li diffusion step alone, a fact which only illustrates that a fraction of the complexes avoids being neutralised by Li during the rapid quenching process.

Finally we emphasise the results from Table IB that Li diffusion at 400-500 °C also creates V_{Ga} and Ga_{As}. In this case we know that annealing alone neither gives the observed hole conductivity nor the bound exciton lines attributed by Yu et al. [16] to the V_{Ga}-Ga_{As} pair. Our experiments do not contradict the excitons being bound to defects involving V_{Ga} or Ga_{As}. As pointed out earlier, however, we do not find it likely that the bound excitons both originate from the same double acceptor [15]. We also emphasise that sample #4 which shows hole conductivity already after the Li diffusion (presumably caused by the Li) also exhibits a reduction of both V_{Ga} and Ga_{As} concentrations. This supports the view that their formation is energetically less favourable in p-type samples.

Conclusions

The intrinsic diffusion coefficient rarely characterises the migration of Li in GaAs due to its strong tendency to react with other defects. We have demonstrated that in highly Li-doped materials complexes containing several Li atoms are formed which strongly impede the migration of Li through the crystal. In our samples a fraction of the lithium can be released from such complexes after surmounting a dissociation energy of 1.20 eV, the majority of the Li atoms being more strongly bound. We have observed significant V_{Ga} and Ga_{As} concentration in samples containing these complexes and demonstrated enhanced concentration of these native defects upon heat treatment. We conclude that Li

forms complexes with these native defects in n type and semi-insulating starting materials and in p-type GaAs:Zn material as well after complete passivation of the Zn acceptors.

In Li-passivated GaAs:Zn, FTIR measurements show that lithium is mainly paired with the Zn acceptors while at low doping levels there is only minimal indication of the association of Li with native defects. After complete passivation of the acceptors, however, complexes of Li and native defects are formed in a similar way as holds for other starting materials. The pairing interaction between Li and Zn is much weaker than that observed in Li-rich material and the original acceptor concentration is easily recovered in ion-drift measurements in the electric field of a Schottky diode. The activation energy for the effective diffusion coefficient is lower than the measured dissociation energy in this case, which illustrates that the pairing interaction is not limiting the diffusion kinetics. Values of the intrinsic diffusivity were determined from the effective diffusivity in this system. We maintain that this data gives the most accurate expression available in the literature for the intrinsic diffusion coefficient of interstitial lithium in GaAs.

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Paper IV

Impurity band in lithium-diffused and annealed GaAs: Conduction and Hall effect measurements,

H. G. Svavarsson
J. T. Gudmundsson
H. P. Gislason

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Impurity band in lithium-diffused and annealed GaAs: Conductivity and Hall effect measurements

H. G. Svavarsson,[1] J. T. Gudmundsson[1,2] and H. P. Gislason[1]
[1]*Science Institute, University of Iceland, Dunhaga 3, IS-107 Reykjavik, Iceland*
[2]*Department of Electrical and Computer Engineering, University of Iceland, Hjardarhaga 2-6, IS-107 Reykjavik, Iceland*
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Originally *n*-type Si-doped GaAs turns *p*-type after Li indiffusion and consequent annealing at 200–600 °C. Temperature-dependent conductivity and Hall effect measurements carried out in the temperature range 30–300 K reveal conduction via impurity bands made up of shallow acceptors in addition to the valence-band conduction. Li diffusion into GaAs reduces the free-carrier concentration which leads to electrical resistivity as high as 10^7 Ω cm. Annealing highly resistive samples at temperatures above 200 °C significantly decreases the room-temperature resistivity to 0.1–1 Ω cm, depending on the annealing temperature. For samples annealed at 300–400 °C we observe a metallic-type conduction which contributes to the conduction even at room temperature. In samples annealed at 500–600 °C the temperature dependence of the resistivity indicates that impurity conduction sets in at temperatures below 100 K. We discuss this conduction change in relation to enhanced gallium vacancy (V_{Ga}) and gallium antisite (Ga_{As}) concentration in Li indiffused and annealed samples.

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I. INTRODUCTION

Doping with lithium is known to reduce the concentration of both holes and electrons in GaAs. Lithium has, similar to hydrogen, a tendency to form complexes with other impurities and native defects when migrating in crystals.[1,2] Suggestion has been made that lithium passivates shallow acceptors in GaAs but compensates shallow donors.[3] It has been demonstrated that annealing of Li-diffused GaAs at 400–500 °C in pure Ga or As atmosphere reduces the Li concentration by about two orders of magnitude.[3,4] This outdiffusion of Li produces *p*-type material, a phenomenon that was first reported by Fuller and Wolfstirn,[5] but the mechanism responsible for the conductivity change has not been identified. The *p*-type conductivity indicates the formation of acceptors which have earlier been related to gallium vacancies.[3,6] Most likely Li exists in GaAs as a substitutional double acceptor Li_{Ga} and as an interstitial donor Li_i which is a fast diffuser.[1] Due to self-compensation of Li in GaAs, one may obtain a high concentration of defects, but yet a low free-carrier concentration. If the impurities are close enough in space, their wave functions may form a band due to overlap. In such an impurity band the holes (or electrons) may travel from one defect center to another without entering the energy bands. This impurity conduction may contribute significantly to the total conductivity, especially at low temperatures. In general, the conductivity can be expressed by

$$\sigma = \sum_{i=1}^{3} \sigma_i^{(0)} \exp[-\epsilon_i/kT], \tag{1}$$

where $\sigma_1 \gg \sigma_2$ or σ_3 and $\epsilon_1 > \epsilon_2 > \epsilon_3$. Here $\sigma_i^{(0)}$ is the extrapolated value of σ_i for $1/T \to 0$. The first term on the right-hand side represents the conduction of free holes in the valence band (for *p*-type material), and it dominates the behavior at higher temperatures. ϵ_1 is the band activation energy which is observed to decrease with increasing acceptor (donor) concentration and to increase with compensation.[7] The third term $\sigma_3^{(0)} \exp(-\epsilon_3/kT)$ describes the hopping conduction of holes as they tunnel from neutral to ionized acceptors in a partially compensated semiconductor. Although the transition is considered to take place by tunneling, an activation energy still exists because of the need to overcome the Coulomb barrier associated with the compensating impurities.[7] The second activation energy ϵ_2 has been interpreted as the energy necessary to place a second hole onto a neutral acceptor and, thus, it increases with increased compensation.[7] This form of impurity conduction only manifests itself with heavier doping.[8] For a semiconductor doped with shallow impurities the $\sigma_3^{(0)} \exp(-\epsilon_3/kT)$ conduction dominates the low-temperature behavior for modest doping (and mandatory compensation). The activation energy ϵ_3 increases rapidly as the compensation $K \to 1$ (or zero) whereas the $\sigma_2^{(0)} \exp(-\epsilon_2/kT)$ increases continuously with compensation.[7] Two major types of hopping mechanism have been identified: nearest-neighbor hopping (NNH) and the variable-range hopping (VRH). When the NNH mechanism dominates, the conduction is proportional to $\exp(-\epsilon_3/kT)$ and the hopping takes place between defects which are close in space but not necessarily in energy. Below a certain critical temperature the hopping process changes from NNH to VRH, where the carrier jumps between more remote defect centers which are close in energy. The VRH has been shown to follow Mott's law which modifies the term $\exp(-\epsilon_3/kT)$ into $\sigma \propto \exp(-T_0/T)^{1/4}$, where T_0 is a constant that includes ϵ_3. Furthermore, Shklovskii and Efros[9] showed that the power term 1/4 in Mott's law should be replaced with 1/2 when electron-electron interaction is taken into account (in the limit of low T). At sufficiently high impurity concentrations N_{crit}, the impurity band merges with the energy band and ϵ_3 and ϵ_2 collapse to zero. This is referred to as metallic conductivity.

In the early 1960s, electric conductivity due to impurity bands was suggested by Olivet[10] to explain the unexpectedly

TABLE I. Data for samples after Li indiffusion at 800 °C and annealing.

Sample	Diffusion	Annealing	ρ [Ω cm]	Carrier [cm^{-3}]	μ_H [cm^2/V s]	K
Ref.	(As-grown)		0.061	$n=2.5\times10^{16}$	4090	
800a	Li 800 °C/4 h	20 °C	$\sim10^7$	$n/p\sim10^{10}$	Unknown	
800b	Li 800 °C/4 h	200 °C/7 h	5×10^2	$p\sim7\times10^{15}$	17	
800c	Li 800 °C/4 h	300 °C/7 h	0.22	$p=4.6\times10^{17}$	62	
800d	Li 800 °C/4 h	400 °C/7 h	0.26	$p=3.5\times10^{17}$	68	
800e	Li 800 °C/4 h	430 °C/7 h	0.035	$p=1.6\times10^{18}$	114	
800f	Li 800 °C/4 h	500 °C/7 h	0.15	$p=3.1\times10^{17}$	133	0.6
800g	Li 800 °C/4 h	600 °C/7 h	0.45	$p=0.7\times10^{17}$	205	0.6

high conduction of n-type GaAs found at low temperature in Hall-effect measurements (< 30 K). A few years later similar results were reported by Emelyanenko and co-workers.[11] By treating the impurity conduction in a similar way as band conduction, they were able to calculate the contribution to the hole concentration from the impurity and valence bands. More recently, Arushanov *et al.* applied this two-band model to p-type β-$FeSi_2$ (Refs. 12 and 13) and p-type $CoSb_3$ (Ref. 14).

Here, we report on the temperature dependence of the conductivity in originally n-type Li-diffused GaAs which was converted to p-type by annealing. Our aim is to confirm the presence of impurity conduction in our samples and to analyze the conduction mechanism. By applying the model of Emelyanenko *et al.* to our data, we are able to distinguish the hole concentration in the valence band from that in the impurity band.

II. SAMPLE PREPARATION AND EXPERIMENT

Horizontal Bridgman-grown n-type Si-doped GaAs with room-temperature electron density $n=2.5\times10^{16}$ cm^{-3} and Hall mobility $\mu_H=4000$ [cm^2/(V s)] was diffused with lithium. The Li indiffusion was made in open quartz ampoules under Ar flow with the samples immersed in Ga melt prepared from 6N Ga metal, GaAs, and about 0.3 wt % of 99.9% Li metal. After the diffusion the samples were cooled to room temperature in the melt.

Two series of samples were made; the first one by indiffusing Li at 800 °C for 4 h and subsequently annealing at various temperatures for 7 h. The second one was made by indiffusing Li at 700 °C for 10 h and annealing at various temperatures for 4 h. Hereafter we will refer to these two series as the 800 and 700 series, respectively. Finally, the samples were polished and etched before Ohmic contacts were made. Zinc-coated gold wire was used for Ohmic contacts. The ohmic contacts were welded directly onto the four corners of the square samples (typical size 3 × 3 mm^2) to avoid heating the samples. Temperature-dependent Hall and conductivity measurements were made on the samples. The Hall coefficient R_H was estimated from the slope of the curve showing Hall voltage versus magnetic field in the range 0–0.75 T. The apparent Hall concentrations were calculated from the Hall coefficient R_H as $n=-r_H/eR_H$ and $p=r_H/eR_H$, respectively, assuming the Hall scattering factor to be isotropic, temperature independent, and of unity value ($r_H=1$). The sample resistance ρ was measured applying the van der Pauw method.

III. EXPERIMENTAL RESULTS

The n-type starting material turns semi-insulating after the Li indiffusion and later p-type as a result of the annealing. Some transport properties measured at room temperature are summarized in Tables I and II. Figures 1(a) and 1(b) show the apparent Hall concentration of holes, p_H, vs $1000/T$ for samples Li indiffused at 800 and 700 °C, respectively, and subsequently annealed at various temperatures. A minimum in the hole concentration curve is seen at roughly 170 K for samples annealed at 300, 400, and 430 °C in Fig. 1(a) but the minima shift towards lower T with increasing annealing temperature. In Fig. 1(b) the minima of the curves appear at roughly $T\approx$ 40 K for all annealing temperatures. Such a well-pronounced minimum in the conduction curve is a characteristic sign of the presence of conduction in a band formed by shallow impurity levels.[11] The slope of the curve for the lowest annealing temperatures in Fig. 1(a) has started to decrease already at room temperature, clearly indicating

TABLE II. Data for samples after Li indiffusion at 700 °C and annealing.

Sample	Diffusion	Annealing	ρ [Ω cm]	Carrier [cm^{-3}]	μ_H [cm^2/V s]	K
Ref.	(As-grown)		0.061	$n=2.5\times10^{16}$	4090	
700a	Li 700 °C/10 h	20 °C	$\sim10^5$	$p\sim1\times10^{15}$	~0	
700b	Li 700 °C/10 h	200 °C/4 h	3.6	$p=1.0\times10^{16}$	173	0.5
700c	Li 700 °C/10 h	250 °C/4 h	0.79	$p=4.6\times10^{16}$	171	0.5
700d	Li 700 °C/10 h	400 °C/4 h	0.064	$p=5.3\times10^{17}$	184	0.5
700e	Li 700 °C/10 h	500 °C/4 h	0.17	$p=1.96\times10^{17}$	184	0.7

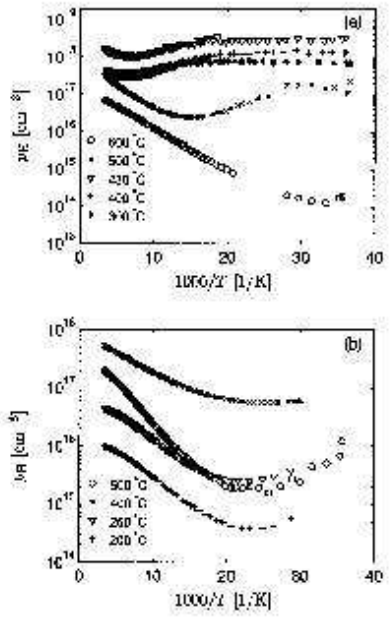

FIG. 1. Temperature dependence of the apparent Hall concentration p_H, for GaAs Li indiffused at (a) 800 °C and (b) 700 °C, and annealed at various temperatures.

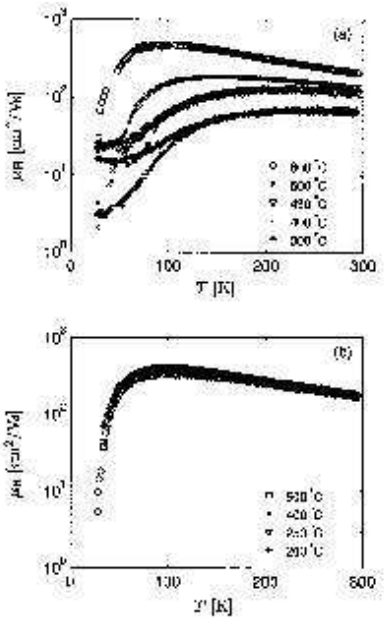

FIG. 2. Temperature dependence of the apparent Hall mobility μ_H for GaAs Li indiffused at (a) 800 °C and (b) 700 °C, and annealed at various temperatures.

impurity conduction even at room temperature. Figures 2(a) and 2(b) show the apparent Hall mobility μ_H vs T for samples Li indiffused at 800 and 700 °C, respectively, and annealed at various temperatures. A noticeable difference is observed. While the mobility is apparently unaffected by the annealing temperature in Fig. 2(b) the opposite is true for Fig. 2(a). Increasing the annealing temperature of the 800 series gradually increases the room-temperature mobility (see also Table I). We also notice that the highest annealing temperature of the 800 series [Fig. 2(a)] results in a mobility curve almost identical to the ones of the 700 series [Fig. 2(b)] over the entire temperature range used. It can therefore be concluded that Li indiffusion at 800 °C creates defects which are not present after Li indiffusion at 700 °C. These defects seem to be Li related since they gradually disappear during Li outdiffusion as the annealing temperature gets higher. We further conclude that the outdiffusion is incomplete at annealing temperatures below 600 °C for the 800 series. A fit $\mu \propto T^{-\alpha}$, above 100 K, to the 600 °C annealing of the 800 series gives $\alpha \sim -1.2$, which is comparable to the $-3/2$ ratio of pure semiconductors. At low temperatures where a $T^{3/2}$ behavior is expected, we observe exponential behavior instead. For the 800 series exponential behavior is seen below $T \approx 70$ K after annealing at 600 and 500 °C but below 160 K after annealing 300–400 °C. For the 700 series exponential behavior was seen below $T \approx 50$ K for all annealing temperatures.

Figure 3 shows the reciprocal temperature dependence of the specific resistivity ρ for the two sample series: Fig. 3(a), Li indiffused at 800 °C, and Fig. 3(b), Li indiffused at 700 °C after annealing at various temperatures. In Fig. 3(a) samples annealed at 300 and 430 °C show a slight increase in the resistivity when T decreases down to ~100 K, where the curve becomes flat and independent of temperature. This plateau, representing zero thermal activation energy, is a clear indication of metallic-type conduction.[15] The sample annealed at 400 °C shows a very similar behavior but the line at low T is not completely horizontal, which reveals a small but nonzero activation energy. The resistivity of this sample only changes from 0.2 to 0.5 Ω cm between 300 and 30 K. In the same temperature regime we observe changes of over three orders of magnitude after annealing at 600 °C and a plateau is never reached. Samples annealed at 500 and 600 °C exhibit curves with two distinct activation energies. The lowest resistivity is obtained after annealing at an intermediate temperature of 430 °C.

The apparent Hall-carrier concentration does not reveal the true concentration in the presence of impurity-band conduction. Simple analysis[12] enables a separation of the hole concentration in the impurity band from that in the valence band. The sum of hole concentrations in the main and impurity bands is assumed to be constant. Following Ref. 12, the ratio of the maxima of the Hall coefficient, $R_{H_{max}}$, and the lowest value of the Hall coefficient at low temperature (freezing region), R_{H_f}, is given by

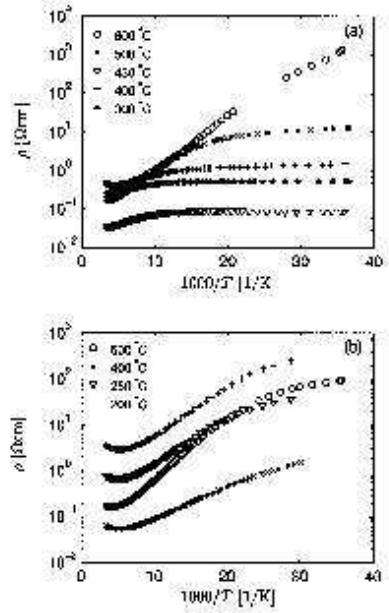

FIG. 3. Temperature dependence of the specific resistivity ρ for GaAs Li indiffused at (a) 800 °C and (b) 700 °C, and annealed at various temperatures.

$$\frac{R_{H_{max}}}{R_{H_t}} = \frac{(b+1)^2}{4b}, \tag{2}$$

$$\frac{R_H}{R_{H_t}} = \frac{(x+b^2)(x+1)}{(x+b)^2}, \tag{3}$$

where $b=\mu_v/\mu_i$ and $x=p_i/p_v$. The subscripts i and v denote impurity and valence bands, respectively. Since the temperature dependence of b is considerable weaker than that of x, b is considered to be a constant. Graphical representation of the dissolved impurity- and valence-band hole concentrations is given in Fig. 4. The activation energy ϵ_i of the acceptor was calculated from the slope of $\ln(\rho T^{3/2})$ vs T^{-1} from the linear curve in Fig. 4. It yields $\epsilon_i = 17$ meV for the sample indiffused at 800 °C and annealed at 500 °C (sample 800f). Samples c, d, and e of the 800 series show metallic behavior and were therefore excluded. In other samples the temperature was never low enough to obtain a distinct minimum in the R_H vs $1000/T$ curve for Eqs. (2) and (3) to be reliable. The transport properties measured at room temperature are given in Tables I and II for the samples indiffused at 800 and 700 °C respectively. From the values of R_{H_d} (the value of R_H as $1/T \to 0$), it is straightforward to calculate the compensation ratio $K=N_d/N_a$, where N_d and N_a are the total concentrations of donors and acceptors, respectively. The room-temperature resistivity ρ of the two sample series,

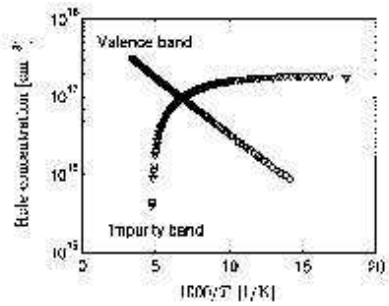

FIG. 4. Hole concentration in the valence and impurity bands for GaAs Li indiffused at 800 °C and annealed at 500 °C.

measured after annealing at different temperatures, is shown in Fig. 5. After Li indiffusion at 700 °C, but prior to annealing, the room-temperature resistivity is on the order of $\rho \sim 10^3$ Ω cm but after the 800 °C indiffusion it is around two orders of magnitude higher, $\rho \sim 10^7$ Ω cm. For different annealing temperatures in the range 200–600 °C the resistivity takes values between $\rho = 5\times10^2$ and 4×10^{-2} Ω cm with a minimum ρ_{min} for annealing temperatures around 400 °C for both sample series. The value of ρ_{min} is similar or even lower than the resistivity of the starting material, in spite of the n- to p-type conversion. The much lower mobility of holes than electrons is compensated for by around a tenfold increment of the carrier concentration. In Fig. 6 the apparent room temperature Hall hole concentration p_H is shown versus the annealing temperature. A maximum in the apparent concentration is seen for both series at similar temperature, roughly around 400 °C, which is a similar temperature that minimizes ρ_{min} in Fig. 5.

IV. DISCUSSION

The Li concentration in GaAs after Li diffusion at 800 °C measured by secondary ion mass spectroscopy (SIMS) is roughly 10^{19} cm^{-3} and has fallen to $\sim 10^{16}$ cm^{-3} after annealing at 400 °C for 20 h.[6] The solid solubility of Li in

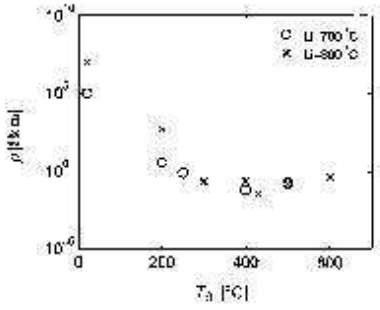

FIG. 5. Specific resistivity at room temperature ρ for Li-diffused GaAs vs annealing temperatures for two sample series: Li indiffused at 700 °C and at 800 °C.

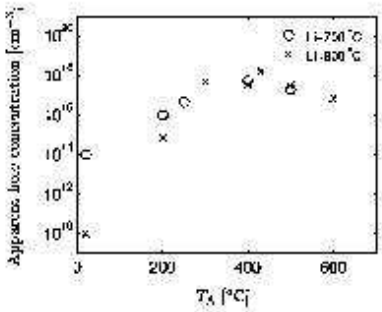

FIG. 6. Apparent Hall hole concentration at room temperature for Li-diffused GaAs vs annealing temperatures for two sample series: Li indiffused at 700 °C and at 800 °C.

GaAs is roughly 10^{16} cm^{-3} at 800 °C and roughly half that value at 700 °C.[5] Hence, we conclude that the total Li concentration in our samples after indiffusion follows the solubility level. A fraction of the Li atoms compensates the donors in the as-grown material (2.5×10^{16} cm^{-3}) but the excess Li compensates or passivates native defects, which leaves the material semi-insulating. Annealing at temperatures above 200 °C releases the lithium from the defect complexes, leaving Ga_{As} and V_{Ga}. Positron annihilation experiments reveal significantly enhanced V_{Ga} and Ga_{As} concentrations in Li indiffused samples, particularly after heat treatment.[6,16] After Li indiffusion at 800 °C for 8 h and subsequent outdiffusion at 400 °C for 7 h the concentrations of the defects were $[Ga_{As}] = 3.2\times10^{17}$ cm^{-3} and $[V_{Ga}] = 7.6\times10^{17}$ cm^{-3}.[16] The first ionization level of the gallium antisite ($Ga_{As}^{0/-}$) is around 78 meV above the valence band and the second one ($Ga_{As}^{-/--}$) is around 204 meV above the valence band.[17] For the gallium vacancy, the first ionization level ($V_{Ga}^{0/-}$) is ~130 meV and the second one ($V_{Ga}^{-/--}$) ~ 490 meV above the valence band.[17] All of these activation energies are high enough to be ruled out as being responsible for the thermally activated conductivity that we observe. Annealing at elevated temperatures under Ga-rich conditions is expected to decrease the V_{Ga} concentration and increase the V_{As} concentration. Due to the vacant As sites, we can expect Ga atoms to jump into the vacancies according to $Ga_{Ga}+V_{As}\rightarrow V_{Ga}+Ga_{As}$. The Ga vacancies created will then (at least partially) be filled by diffusing Ga atoms from interstitial positions, driving the reaction to the right. The presence of the ionized interstitial Li^+ donors interacting with the negatively charged V_{Ga} and Ga_{As} acceptors is believed to stabilize the defect. It has been suggested that during the Li indiffusion the gallium defects are passivated by Li_i, forming neutral defect complexes such as Ga_{As}^{-}-Li^+ and V_{Ga}^{-}-Li^+. In the outdiffusion these pairs break up, releasing V_{Ga} and Ga_{As}, either isolated or as complex defects.[6] The shallow acceptor energy we obtain as 17 meV is lower than the value of ~23 meV reported by Fuller and Wolfstirn[5] (for GaAs diffused by Li at high temperature and subsequently annealed) but may nevertheless reveal the same defect. They attributed this level to a Li^+-Li^{2-} acceptor. However, according to SIMS analysis the remaining Li concentration after annealing is too low for this complex to be responsible for the impurity band. The exponential dependence of the Hall mobility on T at low temperatures for the annealed samples of the 700 series [Fig. 2(b)] clearly indicates a high concentration of charged impurities. A similar behavior is also seen for the highest annealing temperature of the 800 series [Fig. 2(a)]. In fact, all annealed samples of the 700 series have similar mobilities as the one of the highest annealing temperature of the 800 series. We assign this to the originally lower Li indiffused concentration of the 700 series and its longer annealing time (7 h vs 4 h). Hence, the remaining Li concentration after annealing is much higher for the 800 series than for the 700 series, especially at low annealing temperatures. Charged defects, passivated by Li after indiffusion, are thus reactivated at lower annealing temperatures for the 700 series than for the 800 series. Morkoç *et al.* investigated GaAs grown at low temperatures with molecular beam epitaxy.[18] They assumed a power-type dependence of μ_H on T of the form $\mu_H\propto T^{-n}$ at elevated temperatures. At lower temperatures they assumed an exponential dependence of the form $\mu_H\propto \exp(-\epsilon/kT)$ caused by hopping conduction of the nearest-neighbor type. Here, k is the Boltzmann constant and ϵ the thermal activation energy of the hopping Hall mobility. For our data the activation energy ϵ is in the range of 10–20 meV. The resistivity curves in Fig. 3(b) show nonlinear behavior, and the temperature dependence on ρ could not be described by either the $T^{-1/2}$ or the $T^{-1/4}$ behavior. Thus the identification of the mechanism involved is nontrivial. Based on this, we might suggest the thermal activation of the impurity conduction to be of the ϵ_2 type instead of the ϵ_3 type for hopping or even a mixture of those two mechanisms. This can, however, not be true for samples 800c–800e which have flat Hall-concentration curves vs reciprocal T and nonactivated conduction.

Two types of metal-insulator transition (MIT) are commonly recognized: the Mott and Anderson transitions. For low compensation the transition is known to be of Mott type and the critical concentration is given by $N_{crit}\sim(0.25/a_0)^3$ for shallow impurities where a_0 is the Bohr radius of the impurity in question. Using $\epsilon_0=12.85$ and $m^*=0.48m_0$ (the effective mass of holes), in the Bohr radius, we obtain $N_{crit}\sim 5\times10^{18}$ cm^{-3}. When the compensation is strong the MIT occurs at much higher concentration and is referred to as an Anderson transition.[9] We conclude that the critical limit N_{crit} has been reached after indiffusion at 800 °C but not after indiffusion at 700 °C. Samples Li indiffused at 800 °C and annealed at low temperatures had zero activation energy, as clearly visible in Fig. 3(a). This strongly indicates a metallic type of conductivity. After annealing, the effective impurity concentration is lowered and metallic type of conduction is not seen above 430 °C. A distinct minimum in the specific resistivity accompanied with a maximum in the apparent hole concentration was observed after annealing at roughly 400 °C for both sample series. This may be explained by the removal of a Li donor from a neutral defect complex, which competes with the formation of a native donor at elevated temperature. Li readily outdiffuses already at room tempera-

tute but the creation of native defects requires higher temperature. Since the indiffusion and annealing take place under Ga-rich conditions, it would be logical to attribute the defect to V_{As}.

Chen and Spitzer[10] reported Si site switching in originally *n*-type Si-doped GaAs which had been Li indiffused and subsequently annealed. They concluded that the presence of Li could cause the transfer of Si from a Ga lattice site to an As lattice site. The silicon on As site is a shallow acceptor with a typical activation energy of roughly 30 meV or lower in the case of high acceptor concentration. The free-carrier concentration in our as-grown material is 2.5×10^{16} cm^{-3}. This concentration is far too low to account for the impurity band unless we assume high compensation in the as-grown material and consequently much higher total concentration of Si. Si site switching could nevertheless contribute to the carrier concentration observed after Li indiffusion and annealing.

V. CONCLUSION

After Li indiffusion and subsequent annealing, *n*-type GaAs turns *p* type. The conductivity reaches a maximum after annealing at temperature of $\sim$ 400 °C and even exceeds that of the starting material. The results of Hall and conductivity measurements indicate the existence of an impurity band in lithium indiffused and annealed GaAs. This impurity band contributes significantly to the electrical conduction even at room temperature and becomes the dominant transport mechanism at lower temperatures. The concentrations of V_{Ga} and Ga_{As} are significantly enhanced in these samples. However, these defects have levels that are too deep to be responsible for the conduction enhancement. Based on the temperature dependence of the impurity conduction we suggest it to be of metallic type at the lowest annealing temperatures (below 430 °C) for the 800 series but of an intermediate hopping nature after annealing at higher temperatures (above 430 °C). The 700 series seem to belong to the latter for all annealing temperatures.

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Paper V

Frequency-dependent conductivity in lithium diffused and annealed GaAs

J. T. Gudmundsson
H. G. Svavarsson
S. Gudjonsson
H. P. Gislason

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Frequency-dependent conductivity in lithium-diffused and annealed GaAs

J.T. Gudmundsson[a,b,*], H.G. Svavarsson[a], S. Gudjonsson[a], H.P. Gislason[a]

[a] *Science Institute, University of Iceland, Dunhaga 3, IS-107 Reykjavik, Iceland*

[b] *Department of Electrical and Computer Engineering, University of Iceland, Hjardarhaga 2-6, IS-107 Reykjavik, Iceland*

Abstract

We report on measurements of the frequency-dependent conductivity in lithium-diffused (Li-diffused) and annealed GaAs in the frequency range $10–10^6$ Hz and the temperature range 30–300 K. Li diffusion into GaAs reduces the free carrier concentration and can make the material semi-insulating. Using admittance spectroscopy we show that the conduction in semi-insulating Li-diffused GaAs is due to hopping between localized centers. These centers are suggested to be associated with the gallium vacancy V_{Ga} and the gallium antisite Ga_{As}. Furthermore, percolation is apparent in as-diffused samples, indicating that the material contains metallic precipitates. We suggest that the percolation is due to Li precipitation or formation of GaLi clusters during in-diffusion of lithium. At high frequency the AC conductivity is proportional to ω^s. The value of s decreases with increasing temperature which suggests a correlated barrier hopping mechanism.

PACS: 72.20.Ee

Keywords: GaAs; Lithium; AC conductivity; Conductivity measurements; Hopping conduction

1. Introduction

The influence of lithium on the electrical behavior of GaAs has been studied extensively in the past, primarily by Fuller and co-workers [1,2]. It is known that Li diffusion into GaAs reduces the free carrier concentration in undoped, n-type and p-type starting materials [3]. It has been suggested that lithium passivates shallow acceptors in GaAs but compensates shallow donors [4]. The increase in resistivity is roughly 9 orders of magnitude for Li in-diffusion temperatures of 700–800°C [3]. Annealing of lithium-diffused GaAs at 400–500°C in pure Ga or Ar atmosphere reduces the Li concentration by about two orders of magnitude [2,4]. This out-diffusion of Li produces p-type material. This phenomenon was first reported by Fuller and Wolfstirn [1] but the mechanism responsible for the conductivity change has not been fully identified. Temperature dependence of the conductivity suggests that the electron transport occurs via hopping in a partially filled defect band. Annealing in the temperature range 400–450°C leads to metallic-type conduction that is observed even at room temperature. Annealing in the temperature range 500–600°C

*Corresponding author. Tel.: +354-525-4800; fax: +354-552-8911.

E-mail address: tumi@hi.is (J.T. Gudmundsson).

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leads to impurity conduction at temperatures below 100 K [5]. The frequency response of the conductivity is a direct way to characterize different conduction mechanism such as band conduction, hopping between localized centers and percolation. Hopping conductivity is known to exist in molecular beam epitaxy (MBE) GaAs grown at low temperatures [7,8]. Frequency-dependent conductivity measurements have been applied to investigate percolation due to As precipitates in semi-insulating GaAs [9] and in MBE GaAs grown at low temperatures [10]. Here, we report on the temperature dependence of the AC conductivity in originally n-type GaAs that has been Li-diffused and annealed at temperatures below 300°C. The samples investigated here remain semi-insulating and we demonstrate that electron transport occurs via hopping between localized centers and are in some cases due to percolation.

2. Sample preparation and experiment

Horizontal Bridgman grown n-type Si-doped GaAs with room-temperature electron density $n = 2.5 \times 10^{16}$ cm^{-3} and Hall mobility $\mu_H = 4000$ cm^2/V s was diffused with lithium. The Li in-diffusion was made at 800°C in open quartz ampoules under Ar flow with the samples immersed in Ga melt prepared from 6 N Ga metal, GaAs, and about 0.3 wt% of 99.9% Li metal. After the diffusion the samples were cooled to room-temperature in the melt. One sample was baked at 300°C for 10 h. The samples investigated here are listed in Table 1. To make ohmic contacts zinc-coated gold wires were welded directly onto the four corners of the square samples (typical size 3×3 mm^2).

Table 1
Data for samples after Li in-diffusion at 800°C and annealing

Sample	Diffusion	Annealing	ρ (Ω cm)	E_a (meV)
#1	Li 800°C/4 h	300°C/10 h	248	48
#2	Li 800°C/10 h	20°C	1.6×10^5	87
#3	Li 800°C/4 h	20°C	2.4×10^6	240

DC conductivity measurement was made between any two contacts on the sample by applying van der Pauw's method. Admittance spectroscopy measurements were performed using a HP4284A impedance analyzer. The frequency dependence of the AC conductivity was measured at several different temperatures in the range 30–300 K.

3. Results and discussion

The n-type starting material turns semi-insulating after the Li diffusion. The samples used in this study are listed in Table 1. The as-diffused samples have specific resistivity of the order of 10^5–10^6 Ω cm at room temperature. Annealing at 300°C for 10 h decreases the specific resistivity significantly to 248 Ω cm. Fig. 1 shows the specific conductivity of the three different samples. The plots of σ_{DC} versus $1/T$ show a linear behavior in the high-temperature range. The variation of the specific conductivity with $1/T$ indicates an activation energy 48–240 meV from the valence band.

The measured total conductivity $\sigma_{tot}(\omega)$ can be decomposed into two components: a DC component and a frequency-dependent AC component

$$\sigma_{tot}(\omega) = \sigma_{DC} + \sigma_{AC}(\omega), \quad (1)$$

where it is assumed that the two components arise from separate mechanisms. The DC component

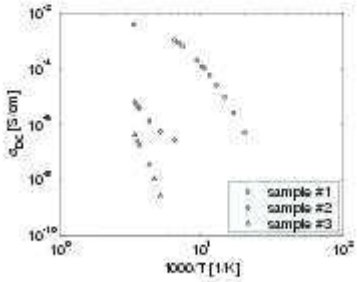

Fig. 1. Specific conductivity for GaAs:Si Li in-diffused at 800°C for 4 h and annealed at 300°C for 10 h (sample #1), Li in-diffused for 10 h (sample #2) and Li in-diffused for 4 h (sample #3). The activation energies are 48, 87 and 240 meV, respectively.

corresponds to band conduction. For convenience, we measure the admittance between two ohmic contacts on the sample. Fig. 2 shows the frequency dependence of the admittance for the three different samples. Fig. 2(a) shows the admittance at various temperatures for GaAs:Si, Li in-diffused at 800°C and annealed at 300°C for 10 h (sample #1). Fig. 2(b) shows the admittance at various temperatures for GaAs:Si, Li in-diffused at 800°C for 10 h (sample #2), and Fig. 2(c) shows the admittance at various temperatures for GaAs:Si, Li in-diffused at 800°C for 4 h (sample #3).

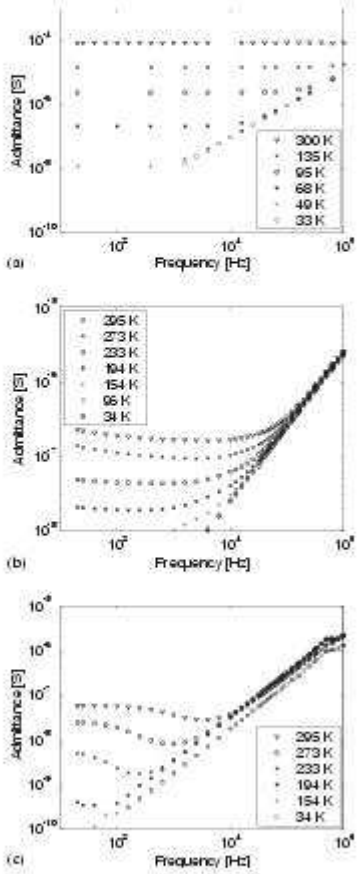

Fig. 2. The admittance versus frequency at various temperatures for GaAs:Si; (a) Li in-diffused at 800°C for 4 h and annealed at 300°C for 10 h, (b) Li in-diffused at 800°C for 10 h (sample #2) and (c) Li in-diffused at 800°C for 4 h (sample #3).

The plot of $\log(\sigma_{AC}(\omega))$ versus $\log\omega$ emphasizes generally two regimes; an essentially flat response at lower frequencies and a crossover to a nearly linear rise with frequency or dispersion. The AC conductivity due to hopping is known to have the form [11]

$$\sigma_{AC}(\omega) = A\omega^s, \tag{2}$$

where A is a constant dependent on temperature, ω is the angular frequency of the AC signal and the exponent s is generally less than or equal to unity. This regime is attributed to hopping conduction and at high enough frequency the admittance is larger than the admittance due to band conduction. The two regimes are clearly visible for sample #1 and hopping conduction sets in at temperatures below 100 K as seen in Fig. 2(a). The frequency-dependent admittance measured in sample #3 exhibits a minimum at a certain frequency ω_m as seen in Fig. 2(c). This minimum in admittance is an indication of percolation. We see a direct relationship between ω_m and the DC admittance as to be expected in the occurrence of percolation [10].

The temperature dependence of the frequency exponent s for the three samples is shown in Fig. 3. The frequency exponent was obtained from straight-line fits in the dispersion regime. The frequency exponent decreases smoothly with increasing temperature and is independent of frequency in the investigated frequency range. The correlated barrier hopping (CBH) model describes charge carrier hops between sites over the potential barrier separating them and predicts that s decreases with increasing temperature [12]. We conclude that the variation of s with temperature suggests that the AC conduction mechanism can be described by the CBH model.

The Li concentration in GaAs after Li diffusion at 800°C measured by secondary ion mass spectroscopy (SIMS) is roughly 10^{19} cm^{-3} and has fallen to $\sim 10^{16}$ cm^{-3} after annealing at 400°C

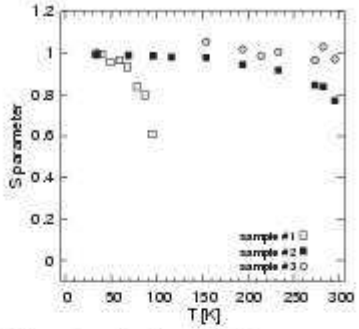

Fig. 3. Temperature dependence of the frequency exponent s for samples #1, #2 and #3.

for 20 h [6]. A fraction of the Li atoms compensates the donors in the as-grown material (2.5×10^{16} cm^{-3}) but the excess Li auto-compensates or neutralizes native defects, which leaves the material semi-insulating. Annealing releases the lithium from the defect complexes, leaving Ga_{As} and V_{Ga} [6,13]. After Li in-diffusion at 800°C for 8 h and subsequent out-diffusion at 400°C for 7 h the concentration of the defects were $[Ga_{As}] = 3.2 \times 10^{17}$ cm^{-3} and $[V_{Ga}] = 7.6 \times 10^{17}$ cm^{-3} [13]. The measured activation energy is in the range 48–240 meV for the as-diffused and annealed samples discussed in this work. Annealing at 400–430°C resulted in metallic-type conduction [5]. A native single acceptor located 68 meV above the valence band edge and believed to be due to the V_{Ga}-Ga_{As} pair in p-type GaAs is known to exist in Ga-rich GaAs [14]. We suggest that the conduction mechanism is related to the V_{Ga}, Ga_{As} or the V_{Ga}–Ga_{As} pair.

Evidence for a percolation regime can be found in the existence of a minimum in the frequency response of the admittance at a given temperature [9,10]. We observe such minima in the as-diffused samples. Percolation indicates that the material contains insulating regions, of large dimensions compared to the electron diffusion length. We suggest that the percolation is due to Li precipitation or formation of GaLi clusters during in-diffusion of lithium. Such precipitation is in the form of small clusters finely distributed in the matrix. Preliminary transmission electron microscope study indicates the presence of GaLi precipitates in the material after in-diffusion at 800°C [15]. These metal precipitates act as Schottky barriers and induce space charge regions around them. This phenomena has been observed in semi-insulating low-temperature MBE grown GaAs [16]. When these depleted regions overlap, electron transport becomes impossible. Percolation is expected if metallic precipitates led to depleted regions around which electron transport occurs. The percolation disappears with annealing and longer in-diffusion time.

4. Conclusion

We report on measurements of the frequency-dependent conductivity in lithium-diffused and annealed GaAs. Li diffusion into GaAs reduces the free carrier concentration and can make the material semi-insulating. We demonstrate that the conduction in semi-insulating Li-diffused GaAs is due to hopping between localized centers. We suggested the centers to be associated with the gallium vacancy and the gallium antisite. Furthermore, percolation is apparent in as-diffused samples indicating that the material contains metallic precipitates and buried Schottky depletion regions. We suggest that the percolation is due to Li precipitation or formation of GaLi clusters during in-diffusion of lithium. At high frequency the AC conductivity is proportional to ω^s. The value of s decreases with increasing temperature suggesting correlated barrier hopping mechanism.

Acknowledgements

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Paper VI

Lithium-diffused and annealed GaAs: Admittance spectroscopy study

H. G. Svavarsson
J. T. Gudmundsson
H. P. Gislason

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Lithium-diffused and annealed GaAs: Admittance spectroscopy study

H. G. Svavarsson[a], J. T. Gudmundsson[a,b] and H. P. Gislason[a]

[a]*Science Institute, University of Iceland,*

Dunhaga 3, IS-107 Reykjavik, Iceland

[b]*Department of Electrical and Computer Engineering,*

University of Iceland, Hjardarhaga 2-6, IS-107 Reykjavik, Iceland

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Abstract

We study lithium-diffused and annealed GaAs by admittance spectroscopy in the frequency range $10 - 10^6$ Hz and the temperature range $30 - 300$ K. Li diffusion turns the GaAs semi-insulating but subsequent out-diffusion of Li increases the conductivity and makes the samples p-type. It is demonstrated that the conduction in semi-insulating Li-diffused GaAs is due to thermally activated carriers in the valence-band percolating around insulating metallic precipitates. At high frequencies the AC conductivity is proportional to ω^x, with x being close to unity value, independent of temperature. We suggest that the percolation may be due to metallic precipitates formed during in-diffusion of lithium and following cooling. After subsequent annealing the AC conductivity becomes proportional to ω^s at high frequencies with the value of s decreasing with increasing temperature. The temperature dependency of s suggests a correlated barrier hopping mechanism in a band of defects. We attribute these defects to gallium vacancies V_{Ga} and gallium antisites Ga_{As}.

I. INTRODUCTION

Although the effect of Li on the electrical properties of GaAs has been investigated intensively through the last four decades many questions still remain to be answered regarding the conduction mechanism [1–4]. It is known that Li diffusion into GaAs reduces the free carrier concentration which leads to electrical conductivity as low as 10^{-7} $\Omega^{-1}\mathrm{cm}^{-1}$ in undoped, n-type and p-type starting materials [4]. Lithium has a strong tendency to form complexes with other impurities and native defects when migrating in crystals [5]. 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 [1, 6]. However, the most weakly bonded Li is removed by annealing at temperature as low as $\sim$ 100°C [7]. The out-diffusion of Li atoms produces p-type material, a phenomenon first reported by Fuller and Wolfstirn [2], but the mechanism responsible for the conductivity change has not been identified. The resulting p-type conductivity indicates the formation of acceptors which have earlier been assigned to gallium vacancies [6, 8]. Temperature dependance of the conductivity suggests that under certain conditions the electron transport occurs via hopping in a partially filled defect-band [3, 9]. Annealing in the range 300 – 400°C leads to hopping conduction which is observed up to room temperature, whereas annealing in the temperature range 400 – 450°C leads to quasi-metallic conduction [3]. After annealing above 600°C the conductivity is controlled by thermally activated valence-band conduction [3].

Admittance spectroscopy is commonly used to probe the periodic electrical current response of devices and electron states in semiconductors when they are stimulated by a small alternating voltage. As such it is a direct way to characterize different types of conduction mechanism such as band-conduction, hopping between localized centers and percolation. The measurement is essentially that of electrical impedance and presents variations of a real and imaginary component, each of which forms a frequency spectrum. At low frequencies the admittance consists of a purely real part (conductance) but at high frequencies the admittance reduces to a purely imaginary part (susceptance) [10]. If the AC and DC conduction is due to (completely) different processes then the measured total conductivity at particular angular frequency ω and temperature, $\sigma_{\mathrm{tot}}(\omega)$, can be decomposed into two components [11],

$$\sigma_{\mathrm{tot}}(\omega) = \sigma_{\mathrm{DC}} + \sigma_{\mathrm{AC}}(\omega). \tag{1}$$

where σ_{DC} and $\sigma_{AC}(\omega)$ are the DC and frequency-dependent (AC) conductivities, respectively. Band-conduction (valence- or conduction-band) is characterized by a relaxation time τ which describes collisions with phonons and affects the band admittance σ_b as [10]

$$\sigma_b(\omega) = \sigma_b(0)\left(\frac{1+i\omega\tau}{1+\omega^2\tau^2}\right). \tag{2}$$

Here, $\sigma_b(0)$ is the admittance at zero frequency which resembles the DC conductivity. The AC conductivity due to hopping is known to have the form [12]

$$\sigma_{AC}(\omega) = A\omega^s \tag{3}$$

where A is a constant and s is a parameter with value between 0 and 1. In the very high frequency limit, electrons hop back and forth between pairs of sites for which the pair transition rates are approximately equal to the frequency [12]. Hence, this applies to situations similar to hopping of carriers between neutral and ionized defect centers in a band of defects. Transport of free carriers (electrons in a conduction band or holes in a valence band) limited by small insulating regions finely distributed in the crystal can also be described by the percolation theory but in a more macroscopical way. In such a case the semiconductor can be considered to be a composite of insulating regions around which the carriers can move. Metallic precipitates in a semiconductor may behave as buried Schottky barriers with overlapping spherical depletion regions [13]. When the depletion regions overlap only partially the conductivity will be affected by percolation behavior and will likely lead to hopping-like conductivity at low temperatures [13]. Thus, admittance spectroscopy is especially suitable for materials in which the conductivity can be described by carriers percolating through conducting paths in an insulating matrix [10, 14].

Admittance spectroscopy has, in the past, been applied to study percolation due to As precipitates in semi-insulating GaAs [14] and in GaAs grown at low-temperature by molecular beam epitaxy [10]. Furthermore, percolation, attributed to metallic precipitates, has been observed in melt-grown GaAs after Li-diffusion at 800°C [15]. Here, we report on the temperature dependence of the AC conductivity in originally n-type and p-type GaAs samples which were lithium-diffused at 800°C and annealed at temperatures below 300°C. We demonstrate that electron transport occurs either via hopping between localized centers or charges percolating around macroscopic insulating regions. We show that both systems respond to an alternating current in a similar way as will be shown in our result.

II. SAMPLE PREPARATION AND EXPERIMENT

Horizontal Bridgman grown Si-doped GaAs and Zn-doped GaAs samples were diffused with Li. The Si-doped starting material had room-temperature carrier concentration $n = 2.5 \times 10^{16}$ cm^{-3} and Hall mobility $\mu_H = 4000$ [cm^2/Vs] while the corresponding values for the Zn-doped GaAs were $p = 2 \times 10^{16}$ cm^{-3} and $\mu_H = 300$ [cm^2/Vs]. The Li diffusion was made at 800°C for 4 and 8 h in open quartz ampoules under Ar flow with the samples and a piece of Li 99.9% metal immersed in a 6N Ga melt. The amount of Li was adjusted to be about 0.3 wt % of the melt. After Li-diffusion the samples were cooled to room-temperature in the melt. Pieces of the as-diffused samples were baked at 300°C and 230°C for 10 h. The samples investigated are listed in table I. Finally, the samples were polished and etched before ohmic contacts were made. To avoid heating the whole sample, ohmic contacts were made by direct welding of Zn-coated gold wires onto the four corners of the square samples (typical size 3×3 mm^2) .

DC conductivity measurements were made between any two contacts on the sample by applying van der Pauw's method. Admittance spectroscopy measurements were performed using a HP4284A impedance analyzer. The frequency dependence of the AC conductivity was measured at several different temperatures in the range 30-300 K. For convenience the impedance analyzer was connected between two of the ohmic contacts in opposite corners. Temperature-dependent Hall and conductivity measurements were made on the most highly conductive sample (sample #4). The Hall coefficient R_H was estimated from the slope of the Hall voltage versus magnetic field in the range 0 – 0.5 Tesla. The apparent Hall concentrations were calculated from the Hall coefficient R_H as $p = r_H/eR_H$ assuming the Hall scattering factor to be isotropic, temperature independent and of unity value ($r_H \equiv 1$).

III. EXPERIMENTAL RESULTS

The room temperature transport properties of the four samples investigated are summarized in Table I. Sample #2 is a piece taken of sample #1 and annealed and sample #4 is similarly a piece taken of sample #3 and annealed. Both the n-type and the p-type starting materials turn semi-insulating after the Li diffusion. A subsequent annealing of the samples leaves them p-type in both cases, as manifested by Hall-measurements. The as-diffused

samples have specific resistivity ρ_{DC} of the order of 10^6 Ωcm at room temperature but this value is significantly reduced by the annealing. Annealing the Zn-doped sample at 230°C for 10 h decreases the resistivity to 1.1 Ωcm whereas annealing the Si-doped samples at 300°C for 10 h reduces the resistivity to 250 Ωcm. In Fig. 1(a) the frequency dependency of the admittance is shown for sample #1 while similar graph for sample #2 is shown in Fig. 1(b) to illustrate the effect of annealing on the n-type starting material. Both figures do in general emphasize two regimes; an essentially flat response at lower frequencies and a cross-over to a nearly linear rise with frequency (dispersion regime). A striking difference between the two samples is manifested in the admittance minima of the as-diffused sample #1, which disappears upon annealing. The frequency at which the minima occurs, ω_m, increases with increasing temperature. A corresponding graph for the p-type starting material before and after annealing, sample #3 and sample #4, is shown in Figs. 2(a) and 2(b), respectively. There we observe features similar to those exhibited for samples #1 and #2 except that the dispersion regime of the annealed sample #4 is not reached at the highest frequency investigated.

Fig. 3 shows the temperature dependence of the admittance for sample #2. At low temperature the conductivity is almost constant but at sufficiently high temperature the conductivity approaches the DC conductivity. It is also clearly seen that the lower the frequency the more the admittance resembles the DC conductivity. A straight-line fit to the high temperature regime (the DC conductivity) of Arrhenius plots gives activation energies 290 and 230 meV for the as-diffused samples #1 and #3 and 48 and 14 meV for the annealed samples #2 and #4, respectively. From Hall measurements the slope of $\ln(pT^{-3/2})$ vs T^{-1} gives a value of 35 meV for sample #4, which was the only sample with low enough conductivity for temperature dependent Hall measaurements.

IV. DISCUSSION

The solid solubility of Li in GaAs is roughly 10^{19} cm^{-3} at 800°C [2]. After Li diffusion at 800°C the total Li concentration, measured by secondary ion mass spectroscopy (SIMS), is roughly 10^{19} cm^{-3} but decreases to $\sim 10^{16}$ cm^{-3} after annealing at 400°C for 20 h [8]. Since the samples investigated in this study are Li-diffused at 800°C for a prolonged period of time the solubility level is expected to indicate the concentration of Li atoms or ions in

the as-diffused samples. A fraction of the Li atoms is expected to compensate the original dopant of the as-grown material ($\sim 2\times10^{16}$ cm^{-3}) but the excess Li neutralizes native defects or auto-compensates, which leaves the material semi-insulating. It has been suggested that lithium passivates shallow acceptors in GaAs but compensates shallow donors [6]. SIMS measurements have shown that after Li in-diffusion at 800°C for 8 h and subsequent out-diffusion at 400°C for 7 h the concentrations of the [Ga_{As}] and [V_{Ga}] defects are 3.2×10^{17} cm^{-3} and 7.6×10^{17} cm^{-3}, respectively [16]. The presence of ionized interstitial Li^+ donors is believed to stabilize the gallium-antisite and the gallium-vacancy by forming neutral complexes such as Ga^-_{As}-Li^+ and V^-_{Ga}-Li^+ [8]. During the out-diffusion of Li, or annealing, these pairs break up, leaving Ga_{As} and V_{Ga}, either isolated or as complex defects [8].

By looking at Figs. 1–3, we see that the DC conductivity is a much stronger function of temperature (exponential) than the AC conductivity (a power law) which emphasizes that a different mechanism is at work in these two regimes. It can also be seen from Figs. 1 and 2 that the dispersion sets in at frequency proportional to the DC conductivity.

In p-type material, whose conductivity is governed by conduction in a defect-band, a consequence of the variation in the acceptor-acceptor separation is that some paths, for a hole travelling between two contacts, are open while others are closed. The general motion of a carrier in the defect-band, in the presence of an electric field, is then in the nature of a percolation process. As a result of the percolation current flow, only a part of the total volume contributes to the (low temperature) DC conduction. Therefore the contributing volume of the samples, and hence the conductivity, can be increased dramatically with alternating current [17]. As the temperature increases and the defects are ionized, conventional band-conduction gradually takes over and becomes the dominating conduction mechanism usually well below the room temperature. The band-conduction is considered to be more or less independent of frequency, in contrast to conduction mechanism such as percolation. In a macroscopic percolation system the conductivity is only a function of the dimension of the system and thus can be expressed in terms of a scaling law $\sigma \propto \omega^x$ with a universal exponent x [10]. A closer look at the data shows that the temperature dependence of the frequency exponent is different for the as-diffused samples and the annealed samples. Therefore, different exponents are defined for these two cases. In case of the as-diffused samples we refer to the exponent as x, but after subsequent annealing we refer to it as s. The values of the exponent x for the as-diffused samples #1 and #3, shown in Fig. 4, were obtained from

straight-line fits in the high frequency dispersion regime shown in Figs. 1(a) and 2(a). We found that x had a constant value close to unity throughout the whole temperature regime investigated. However the exponent s, for the annealed sample #2, shows a very strong temperature dependence, as seen in Fig. 5.

A. Percolation

The existence of a macroscopic percolation regime in the as-diffused samples #1 and #3 is explored further in Fig. 6 where a linear relationship between ω_m and σ_{DC} (the flat part of the admittance) is seen, which is clear indication of a conduction by carriers percolating around macroscopic insulating regions. It may therefore be concluded that metallic precipitation is present after the Li diffusion at $T = 800°C$ and subsequent quenching to room temperature. In an admittance spectroscopy study of low-temperature grown GaAs, Khirouni et al. attributed a distinct minimum in the $\sigma(\omega)$ curve to a percolation regime caused by precipitation of As in a metallic-like islands [10]. A similar minimum is seen in our Figs 1(a) and 2(a). We suggest that the percolation may be due to GaLi precipitation during in-diffusion of Li and subsequent cooling to room temperature. Preliminary transmission electron microscope study on GaAs after Li-diffusion at 800°C revealed a lattice dimension of clusters which matched that of a GaLi crystal while the existence of As and Li precipitates were ruled out [18]. A precipitation of GaLi would be in the form of small clusters finely distributed in the matrix which would act as Schottky barriers and induce space charge regions around them. Such buried Schottky barriers with overlapping spherical depletion regions have been observed in semi-insulating low temperature MBE grown GaAs [13]. Based on the idea of Sarychev and Brouers [19], of hopping-assisted tunneling, Khirouni et al. [10] derived the following equation for the frequency-dependent admittance in a macroscopic percolation system;

$$\sigma(\omega) = \sigma(0)\frac{\sqrt{1+\omega^6\theta^6}}{1+\omega^2\theta^2} \tag{4}$$

in which τ has been replaced by θ, a macroscopic relaxation time characterizing the electron scattering by insulating (depleted) regions around which the electrons percolate. When these depleted regions overlap, the transport of carriers is retarded. A plot of $\sigma(\omega)$ given by equation (4) exhibits a minimum for the frequency ω_m, where $\omega_m\theta = 0.856$ [10]. A

combination of the simple relation $\omega_m\theta = 0.856$, and the data of Figs. 1(a) and 2(a) is used to probe the temperature dependence of θ. An Arrhenius plot of θ for samples #1 and #3, shown in Fig. 7, indicates that θ is an exponential function of the inverse temperature. A straight-line fit to the data according to

$$\theta \propto \exp(\Delta E/k_B T),$$

gives the activation energy $\Delta E \sim 340$ and 200 meV, for samples #1 and #3, respectively. These values should correspond to the thermal activation energies of 290 and 230 meV obtained from the DC conductivity [20, 21] for samples #1 and #3, respectively, and in fact the energies are in qualitative agreement with each other.

B. Hopping conductivity

The values of the exponent s for sample #2, shown in Fig. 5, were obtained from a straight-line fit in the high frequency dispersion regime shown in Fig. 1. It was not possible to obtain values of s for the other annealed sample, #4, since the conductivity had a constant value throughout the whole frequency regime investigated, even at the lowest temperature (36 K). A strong temperature dependence of s is observed. The value decreases with increasing temperature, from being close to unity at the lowest temperature, which suggests that the AC conduction mechanism can be described by hopping of carriers between localized centers in accordance with the correlated barrier hopping (CBH) model. A polynomial fit to the values of s for sample #2 (in Fig. 5) gives the value of $T = 107$ K at $s = 0$. This indicates that hopping-conduction sets in below ~ 110 K, which is in good agreement with previous experiments on Li-diffused and annealed GaAs [9]. Based on this and the observed activation energies of 14–48 meV we conclude that the defect-band in the annealed samples is made up of shallow acceptors 20–50 meV above the valence-band.

The physical meaning of the activation energies 290–340 and 200–230 meV, of the as-diffused samples #1 and #3, is not clear. One interpretation would be the presence of deep Li-related acceptors with a very small concentration (keeping in mind that the resistance of the as-diffused samples are 4-6 orders of magnitude higher than that of the annealed samples). Hopping conduction is impossible in an empty or a full defect-band. All native defects and impurities in the samples are neutralized by Li during the Li-diffusion phase,

which explains why no hopping-conduction is observed prior to annealing. After annealing a portion of the Li is removed, creating a partially filled defect-band, in view of the hopping-conduction observed. A native single acceptor located 68 meV above the valence-band edge in $p-$type GaAs is known to exist in Ga-rich GaAs and is believed to be due to the V_{Ga}-Ga_{As} pair [22]. $Ga_{As}^{0/-}$, $Ga_{As}^{-/--}$ and $V_{Ga}^{0/-}$ have energy levels 80, 200 and 140 meV above the valence band, repectively [23]. Zn is a typical shallow acceptor in GaAs with a level $\sim$ 35 meV above the valence-band. However, a band of such defects would be closer to the valence-band due to band-broadening.

The CBH model describes charge carrier hops between sites over the potential barrier separating them [24]. For single polaron hopping the barrier height, W, is related to the distance between the hopping sites R as:

$$W(R) = W_m - \frac{e^2}{\pi\epsilon\epsilon_0 R}, \tag{5}$$

where W_m is the maximum barrier height (i.e. at infinite site separation) and ϵ the bulk dielectric constant. In the case of classical hopping of carriers over a potential barrier W separating two energetically favorable sites the relaxation time is

$$\tau = \tau_0 \exp(W/k_B T) \tag{6}$$

where τ_0 is a characteristic relaxation time (assumed to be an inverse optical phonon frequency $\sim 10^{-13}$ s) [24]. Based on the CBH model, the frequency exponent s depends on the temperature as [24]

$$s = 1 - \frac{6k_B T}{W_m + k_B T \ln(\omega\tau_0)}. \tag{7}$$

When $W_m \gg k_B T$ the frequency exponent s is practically independent of frequency and mainly dependent on temperature. When obeying this law, the hopping regime can easily be recognized by the temperature dependence of s; the value of s should decrease with increasing temperature. In Fig. 5 equation (7) is fitted to our data using W_m as the fitting parameter, $\omega = 10^6$ s^{-1} and $\tau_0 = 10^{-13}$ s (the dotted line). The closest fit was obtained with $W_m = 230$ meV but the result was at its best only in fair agreement with our data.

The CBH model assumes randomly distributed defect centers, but if one assumes paired defects instead equation (7) has to be modified. A correction term of the form T/T_0, where T_0 is a constant associated with a transition to a different conduction mechanism, may be added to equation (7). A similar modification has been done for chalcogenic glasses where T_0

is associated with the glass-transition temperature [24]. The equation can then be written as

$$s = 1 - \frac{6k_B T}{W_m + k_B T \ln(\omega\tau_0)} + \frac{T}{T_0}. \quad (8)$$

By using $T_0 = 350$ K, $W_m = 230$ meV and $\omega\tau = 10^{-7}$, we obtain a reasonable good fit to the data represented in Fig. 5 as shown by the solid line. The physical interpretation of such a correction-term in our case is, however, vague and should be taken with precaution.

To summarize, deep defects located 200-340 meV above the valence-band are created during diffusion of Li into GaAs. During cooling of the as-diffused samples a metallic precipitation occurs. Hence the conduction mechanism in the as-diffused samples is characterized by thermally activated holes percolating around insulating regions of the metallic precipitates. In the annealing process a portion of the Li is removed and a partially filled band of shallow defect-levels, whose wavefunctions overlap, is invoked. This gives rise to a hopping-conduction mechanism which dominates the conductivity below roughly 100 K.

V. CONCLUSION

We report measurements of the frequency-dependent conductivity in lithium diffused and annealed GaAs. Li diffusion into GaAs reduces the free carrier concentration and makes the material semi-insulating. Positron annihilation spectroscopy shows that both gallium vacancies V_{Ga} and gallium antisite defects Ga_{As} are formed during the in-diffusion of Li and increase in concentration upon out-diffusion of Li (annealing) [16].

We demonstrate that the dominating conduction mechanism in the as-diffused samples is different from that of the annealed samples: After Li-diffusion, the conduction takes place in the valence-band in which free holes, provided by thermal activation of deep-levels, percolate around insulating regions. The presence of percolation indicates that the material contains metallic precipitates and buried Schottky depletion regions. We suggest that the percolation may be due to GaLi, precipitating during in-diffusion of lithium and following cooling. After subsequent annealing the conduction occurs in a partially filled defect-band in which electrons move by hopping between occupied and empty defects. We attribute the defect-band to Ga_{As} and V_{Ga} defects, located 20-50meV above the valence band. At high frequency the AC conductivity is proportional to ω^s. The value of s decreases with increasing temperature suggesting a CBH mechanism. A fit to our data, using the CBH

model, was, however, only in a qualitative agreement with the theory and the possibility of more than one transport mechanisms operating simultaneously should be borne in mind.

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Table I: Data for samples after Li in-diffusion at 800°C and annealing.

Sample	Diffusion	Annealing	ρ [Ωcm]	E_a [meV]
#1 GaAs:Si	Li 800°C/4h	20°C	2.4×10^6	290
#2 GaAs:Si	Li 800°C/4h	300°C/10h	2.5×10^2	48
#3 GaAs:Zn	Li 800°C/8h	70°C/2h	1.0×10^6	230
#4 GaAs:Zn	Li 800°C/8h	230°C/10h	1.1	14 (35)

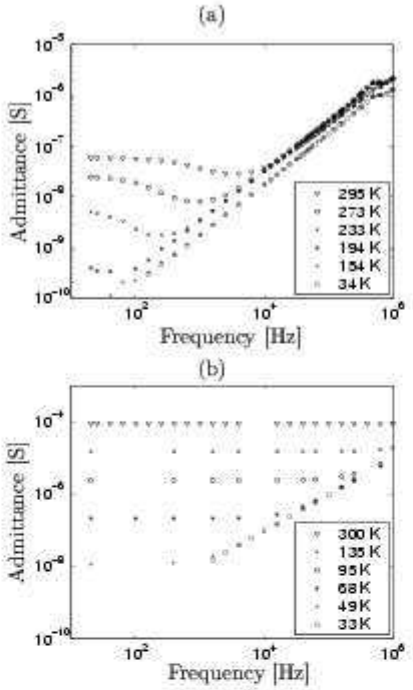

Figure 1: Admittance versus frequency at various temperatures for GaAs:Si; (a) Li diffused at 800°C/4h (sample #1), and (b) after subsequent annealing at 300°C/10h (sample #2).

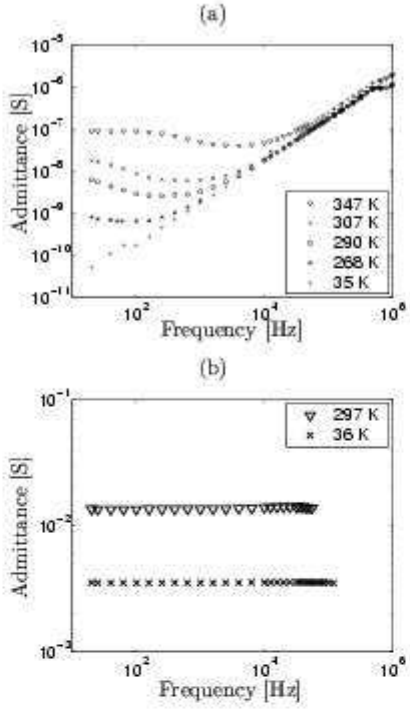

Figure 2: Admittance versus frequency at various temperatures for GaAs:Zn; (a) Li diffused at 800°C/4h (sample #3), and (b) after subsequent annealing at 300°C/10h (sample #4).

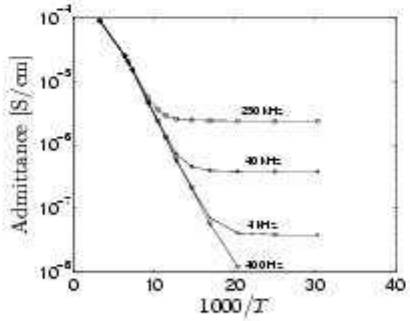

Figure 3: Temperature dependence of admittance for GaAs:Si, Li in-diffused at 800°C for various frequencies and annealed at 300°C for 10 h (sample #2). At low frequency the conductivity compares to conventional DC conductivity.

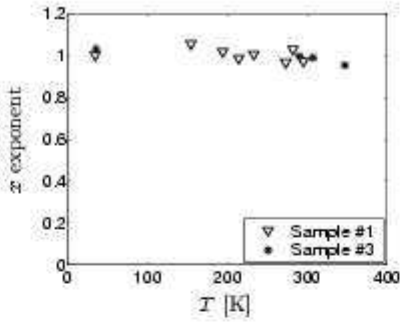

Figure 4: Temperature dependence of the frequency exponent x for the Li in-diffused samples #1 and #3.

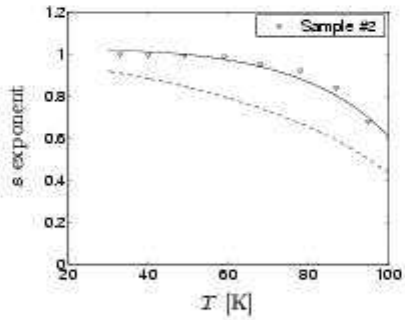

Figure 5: Temperature dependence of the frequency exponent s for Li-diffused and annealed sample (sample #2). The dotted line is a fit plotted from equation (7) with $W_m = 230$ meV and $\omega\tau = 10^6$. The solid line is plotted from modified equation (7).

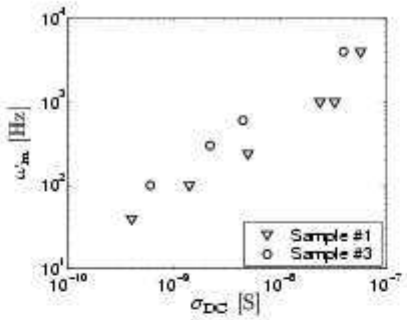

Figure 6: Variation of the frequency at admittance minimum with DC conductivity of the as-diffused samples #1 and #3.

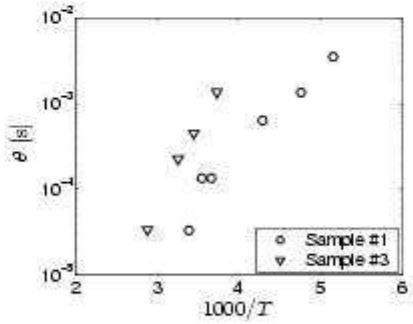

Figure 7: Temperature dependence of the relaxation time θ for the as-diffused samples #1 and #3.