

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

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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  $10^7 \Omega \text{ cm}$ . Annealing highly resistive samples at temperatures above 200 °C significantly decreases the room-temperature resistivity to 0.1–1  $\Omega \text{ cm}$ , 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 ( $V_{\text{Ga}}$ ) and gallium antisite ( $\text{Ga}_{\text{As}}$ ) 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.<sup>1,2</sup> Suggestion has been made that lithium passivates shallow acceptors in GaAs but compensates shallow donors.<sup>3</sup> It has been demonstrated that annealing of Li-diffused GaAs at 400–500 °C in pure Ga or Ar atmosphere reduces the Li concentration by about two orders of magnitude.<sup>3,4</sup> This outdiffusion of Li produces *p*-type material, a phenomenon that was first reported by Fuller and Wolfstirn,<sup>5</sup> 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.<sup>3,6</sup> Most likely Li exists in GaAs as a substitutional double acceptor  $\text{Li}_{\text{Ga}}$  and as an interstitial donor  $\text{Li}_i$  which is a fast diffuser.<sup>1</sup> 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

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

where  $\sigma_1 \gg \sigma_2$  or  $\sigma_3$  and  $\epsilon_1 > \epsilon_2 > \epsilon_3$ . Here  $\sigma_i^{(0)}$  is the extrapolated value of  $\sigma_i$  for  $1/T \rightarrow 0$ . 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.  $\epsilon_1$  is the band activation energy which is observed to decrease with increasing acceptor

(donor) concentration and to increase with compensation.<sup>7</sup> 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.<sup>7</sup> The second activation energy  $\epsilon_2$  has been interpreted as the energy necessary to place a second hole onto a neutral acceptor and, thus, it increases with increased compensation.<sup>7</sup> This form of impurity conduction only manifests itself with heavier doping.<sup>8</sup> 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  $\epsilon_3$  increases rapidly as the compensation  $K \rightarrow 1$  (or zero) whereas the  $\sigma_2^{(0)} \exp(-\epsilon_2/kT)$  increases continuously with compensation.<sup>7</sup> 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  $\epsilon_3$ . Furthermore, Shklovskii and Efros<sup>9</sup> 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  $N_{\text{crit}}$ , the impurity band merges with the energy band and  $\epsilon_3$  and  $\epsilon_2$  collapse to zero. This is referred to as metallic conductivity.

In the early 1960s, electric conductivity due to impurity bands was suggested by Oliver<sup>10</sup> to explain the unexpectedly

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

Sample	Diffusion	Annealing	$\rho$ [ $\Omega$ cm]	Carrier [ $\text{cm}^{-3}$ ]	$\mu_{\text{H}}$ [ $\text{cm}^2\text{V s}$ ]	$K$
Ref.	(As-grown)		0.061	$n=2.5\times 10^{16}$	4090	
800a	Li 800 °C/4 h	20 °C	$\sim 10^7$	$n/p\sim 10^{10}$	Unknown	
800b	Li 800 °C/4 h	200 °C/7 h	$5\times 10^2$	$p\sim 7\times 10^{14}$	17	
800c	Li 800 °C/4 h	300 °C/7 h	0.22	$p=4.6\times 10^{17}$	62	
800d	Li 800 °C/4 h	400 °C/7 h	0.26	$p=3.5\times 10^{17}$	68	
800e	Li 800 °C/4 h	430 °C/7 h	0.035	$p=1.6\times 10^{18}$	114	
800f	Li 800 °C/4 h	500 °C/7 h	0.15	$p=3.1\times 10^{17}$	133	0.6
800g	Li 800 °C/4 h	600 °C/7 h	0.45	$p=0.7\times 10^{17}$	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.<sup>11</sup> 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  $\beta$ -FeSi<sub>2</sub> (Refs. 12 and 13) and  $p$ -type CoSb<sub>3</sub> (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  $n=2.5\times 10^{16}$   $\text{cm}^{-3}$  and Hall mobility  $\mu_{\text{H}}=4000$  [ $\text{cm}^2/(\text{V s})$ ] 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  $3\times 3$  mm<sup>2</sup>) to avoid heating the samples. Temperature-dependent Hall and conductivity measurements were made on the samples. The Hall coefficient  $R_{\text{H}}$  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  $R_{\text{H}}$  as  $n=-r_{\text{H}}/eR_{\text{H}}$  and  $p=r_{\text{H}}/eR_{\text{H}}$ , respectively, assuming the Hall scattering factor to be isotropic, temperature independent, and of unity value ( $r_{\text{H}}\equiv 1$ ). The sample resistance  $\rho$  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,  $p_{\text{H}}$ , 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.<sup>11</sup> 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	$\rho$ [ $\Omega$ cm]	Carrier [ $\text{cm}^{-3}$ ]	$\mu_{\text{H}}$ [ $\text{cm}^2\text{V s}$ ]	$K$
Ref.	(As-grown)		0.061	$n=2.5\times 10^{16}$	4090	
700a	Li 700 °C/10 h	20 °C	$\sim 10^5$	$p\sim 1\times 10^{14}$	$\sim 0$	
700b	Li 700 °C/10 h	200 °C/4 h	3.6	$p=1.0\times 10^{16}$	173	0.5
700c	Li 700 °C/10 h	250 °C/4 h	0.79	$p=4.6\times 10^{16}$	171	0.5
700d	Li 700 °C/10 h	400 °C/4 h	0.064	$p=5.3\times 10^{17}$	184	0.5
700e	Li 700 °C/10 h	500 °C/4 h	0.17	$p=1.96\times 10^{17}$	184	0.7

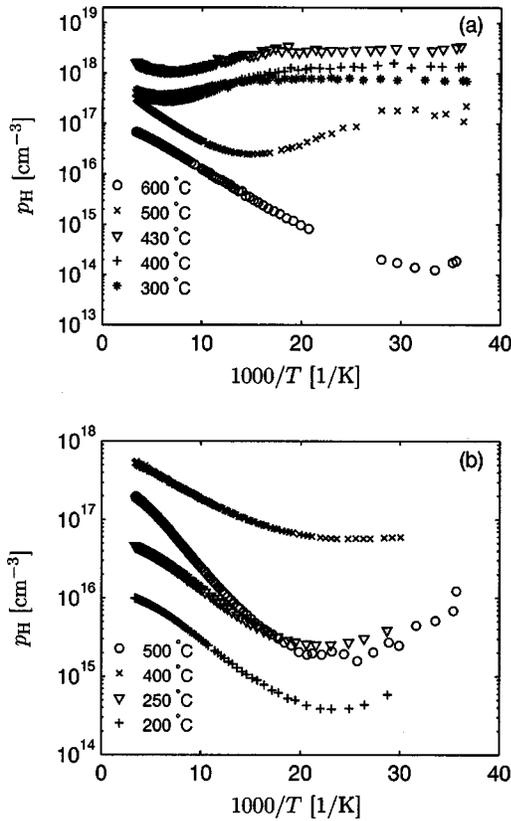


FIG. 1. Temperature dependence of the apparent Hall concentration  $p_H$ , for GaAs Li indiffused at (a) 800 °C and (b) 700 °C, and annealed at various temperatures.

impurity conduction even at room temperature. Figures 2(a) and 2(b) show the apparent Hall mobility  $\mu_H$  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(a) the opposite is true for Fig. 2(b). 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

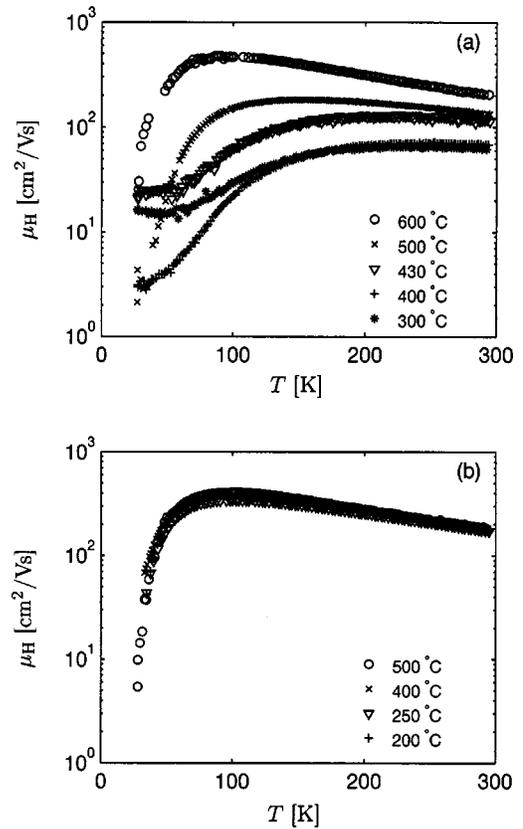


FIG. 2. Temperature dependence of the apparent Hall mobility  $\mu_H$  for GaAs Li indiffused at (a) 800 °C and (b) 700 °C, and annealed at various temperatures.

the specific resistivity  $\rho$  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  $\sim 100$  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.<sup>15</sup> 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  $\Omega$  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<sup>12</sup> 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

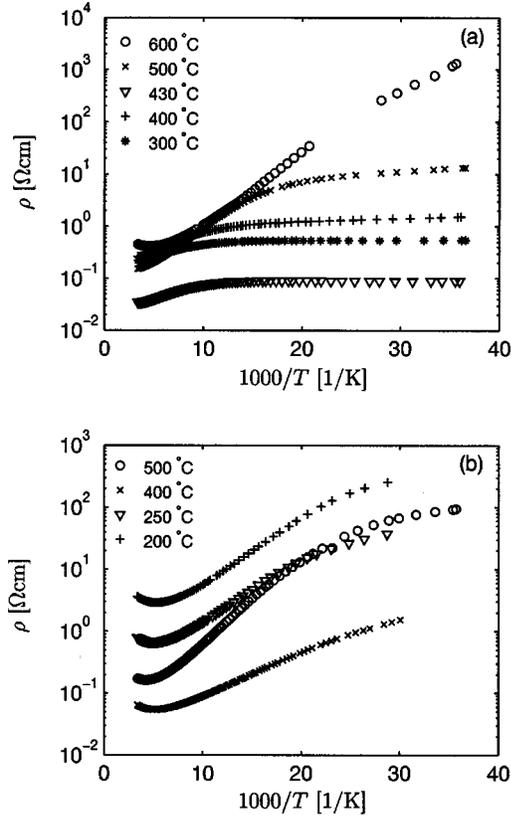


FIG. 3. Temperature dependence of the specific resistivity  $\rho$  for GaAs Li indiffused at (a) 800 °C and (b) 700 °C, and annealed at various temperatures.

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

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

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  $\epsilon_1$  of the acceptor was calculated from the slope of  $\ln(pT^{-3/2})$  vs  $T^{-1}$  from the linear curve in Fig. 4. It yields  $\epsilon_1 = 17$  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  $1/T \rightarrow 0$ ), 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  $\rho$  of the two sample series,

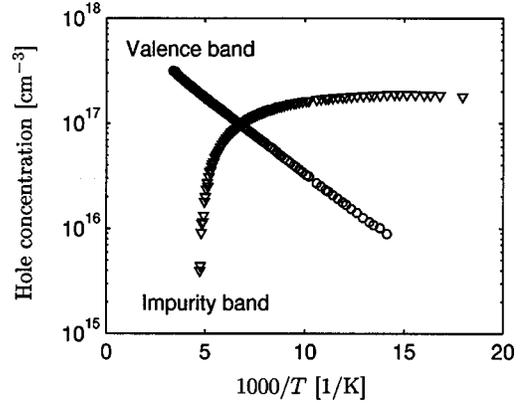


FIG. 4. Hole concentration in the valence and impurity bands for GaAs Li indiffused at 800 °C and annealed at 500 °C.

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  $\rho \sim 10^5 \Omega \text{ cm}$  but after the 800 °C indiffusion it is around two orders of magnitude higher,  $\rho \sim 10^7 \Omega \text{ cm}$ . For different annealing temperatures in the range 200–600 °C the resistivity takes values between  $\rho = 5 \times 10^2$  and  $4 \times 10^{-2} \Omega \text{ cm}$  with a minimum  $\rho_{\min}$  for annealing temperatures around 400 °C for both sample series. The value of  $\rho_{\min}$  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  $\rho_{\min}$  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  $10^{19} \text{ cm}^{-3}$  and has fallen to  $\sim 10^{16} \text{ cm}^{-3}$  after annealing at 400 °C for 20 h.<sup>6</sup> The solid solubility of Li in

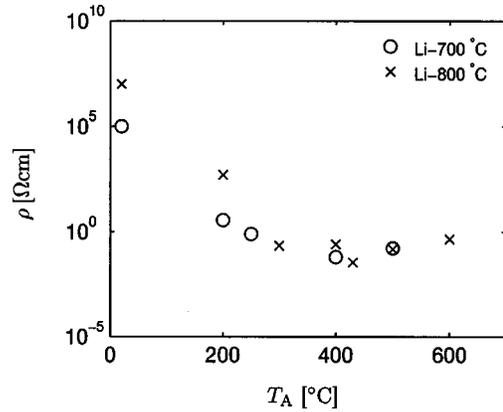


FIG. 5. Specific resistivity at room temperature  $\rho$  for Li-diffused GaAs vs annealing temperatures for two sample series: Li indiffused at 700 °C and at 800 °C.

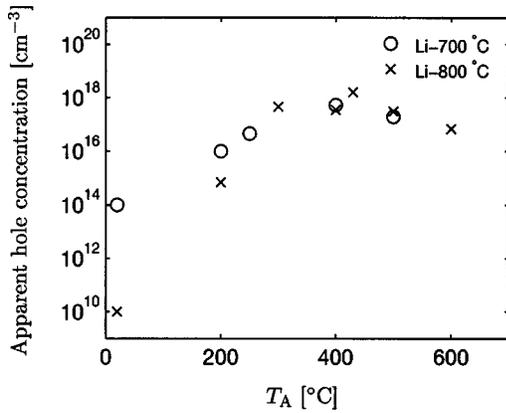


FIG. 6. Apparent Hall hole concentration at room temperature for Li-diffused GaAs vs annealing temperatures for two sample series: Li indiffused at 700 °C and at 800 °C.

GaAs is roughly  $10^{19} \text{ cm}^{-3}$  at 800 °C and roughly half that value at 700 °C.<sup>5</sup> 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 ( $2.5 \times 10^{16} \text{ cm}^{-3}$ ) 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  $\text{Ga}_{\text{As}}$  and  $V_{\text{Ga}}$ . Positron annihilation experiments reveal significantly enhanced  $V_{\text{Ga}}$  and  $\text{Ga}_{\text{As}}$  concentrations in Li indiffused samples, particularly after heat treatment.<sup>6,16</sup> After Li indiffusion at 800 °C for 8 h and subsequent outdiffusion at 400 °C for 7 h the concentrations of the defects were  $[\text{Ga}_{\text{As}}] = 3.2 \times 10^{17} \text{ cm}^{-3}$  and  $[V_{\text{Ga}}] = 7.6 \times 10^{17} \text{ cm}^{-3}$ .<sup>16</sup> The first ionization level of the gallium antisite ( $\text{Ga}_{\text{As}}^{0/-}$ ) is around 78 meV above the valence band and the second one ( $\text{Ga}_{\text{As}}^{-/-}$ ) is around 204 meV above the valence band.<sup>17</sup> For the gallium vacancy, the first ionization level ( $V_{\text{Ga}}^{0/-}$ ) is  $\sim 130$  meV and the second one ( $V_{\text{Ga}}^{-/-}$ )  $\sim 490$  meV above the valence band.<sup>17</sup> 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  $V_{\text{Ga}}$  concentration and increase the  $V_{\text{As}}$  concentration. Due to the vacant As sites, we can expect Ga atoms to jump into the vacancies according to  $\text{Ga}_{\text{Ga}} + V_{\text{As}} \rightarrow V_{\text{Ga}} + \text{Ga}_{\text{As}}$ . 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  $\text{Li}^+$  donors interacting with the negatively charged  $V_{\text{Ga}}$  and  $\text{Ga}_{\text{As}}$  acceptors is believed to stabilize the defect. It has been suggested that during the Li indiffusion the gallium defects are passivated by  $\text{Li}_i$ , forming neutral defect complexes such as  $\text{Ga}_{\text{As}}^- \text{Li}^+$  and  $V_{\text{Ga}}^- \text{Li}^+$ . In the outdiffusion these pairs break up, releasing  $V_{\text{Ga}}$  and  $\text{Ga}_{\text{As}}$ , either isolated or as complex defects.<sup>6</sup> The shallow acceptor energy we obtain as 17 meV is lower than the value of  $\sim 23$  meV reported by Fuller and Wolfstirn<sup>5</sup> (for GaAs diffused by Li at high temperature and subsequently annealed) but may nevertheless reveal the same defect. They

attributed this level to a  $\text{Li}^+ \text{Li}^{2-}$  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. Morvic *et al.* investigated GaAs grown at low temperatures with molecular beam epitaxy.<sup>18</sup> They assumed a power-type dependence of  $\mu_{\text{H}}$  on  $T$  of the form  $\mu_{\text{H}} \propto T^{-n}$  at elevated temperatures. At lower temperatures they assumed an exponential dependence of the form  $\mu_{\text{H}} \propto \exp(-\epsilon/kT)$  caused by hopping conduction of the nearest-neighbor type. Here,  $k$  is the Boltzmann constant and  $\epsilon$  the thermal activation energy of the hopping Hall mobility. For our data the activation energy  $\epsilon$  is in the range of 10–20 meV. The resistivity curves in Fig. 3(b) show non-linear behavior, and the temperature dependence on  $\rho$  could not be described by either the  $T^{-1/2}$  or the  $T^{-1/4}$  behavior. Thus the identification of the mechanism involved is non-trivial. Based on this, we might suggest the thermal activation of the impurity conduction to be of the  $\epsilon_2$  type instead of the  $\epsilon_3$  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  $N_{\text{crit}} \sim (0.25/a_0)^3$  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  $N_{\text{crit}} \sim 5 \times 10^{18} \text{ cm}^{-3}$ . When the compensation is strong the MIT occurs at much higher concentration and is referred to as an Anderson transition.<sup>9</sup> We conclude that the critical limit  $N_{\text{crit}}$  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-

ture 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<sup>19</sup> 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  $2.5 \times 10^{16} \text{ cm}^{-3}$ . 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  $\sim 400^\circ\text{C}$  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  $430^\circ\text{C}$ ) for the 800 series but of an intermediate hopping nature after annealing at higher temperatures (above  $430^\circ\text{C}$ ). The 700 series seem to belong to the latter for all annealing temperatures.

## ACKNOWLEDGMENTS

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