RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 48, NUMBER 16 15 OCTOBER 1993-II

Rapid Communications

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Lithium passivation of Zn and Cd acceptors in *p*-type GaAs

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(Received 25 August 1993)

We report lithium passivation of the shallow acceptors Zn and Cd in *p*-type GaAs which we attribute to the formation of neutral Li-Zn and Li-Cd complexes. Similar to hydrogen, another group-I element, lithium strongly reduces the concentration of free holes when introduced into *p*-type GaAs. The passivation is inferred from an increase of both the hole mobility and the resisitivity throughout the bulk of the sample. It is observed most clearly for Li concentrations comparable to the shallow-acceptor concentration. In addition, compensation of shallow acceptors by randomly distributed donors is present in varying degree in the Li-diffused samples. Unlike hydrogenation of *n*-type GaAs, Li doping shows no evidence of neutralizing shallow donors in GaAs.

Passivation of electrically active defects in semiconductors is characterized by a simultaneous increase of carrier mobility and a reduction of carrier concentration. This effect is caused by the formation of neutral pairs that reduces the carrier concentration as well as the number of ionized scattering centers. In the case of compensation, on the other hand, the reduction of charge carriers is always accompanied by a decrease of the mobility caused by the increase of the number of isolated ionized scattering centers. Hydrogen passivation of shallow and deep impurities is a well-known phenomenon both in elemental and compound semiconductors.[1–5] In particular, in GaAs hydrogen passivates both shallow donors[2] and acceptors.[5] The interaction of hydrogen with defects in crystalline semiconductors has a great technological significance and therefore it has been extensively investigated. Doping of GaAs by other group-I elements, on the other hand, has not been widely used except for fundamental investigations.

In the present paper we focus on the electrical behavior of the group-I element lithium in crystalline GaAs and investigate its effects on shallow donors and acceptors in *n*-type and *p*-type material, respectively. Lithium doping reduces the concentration of both electrons and holes in GaAs and has commonly been used to prepare samples for local vibrational mode (LVM) spectroscopy.[6] Despite extensive studies in the past and spectroscopic evidence for pair formation[6] the question of lithium passivation of shallow dopants as compared to conventional compensation has not been addressed. From the results obtained in this work we conclude that lithium *passivates* shallow acceptors in GaAs but *compensates* shallow donors.

A number of horizontal Bridgman *p*-type GaAs samples with Zn or Cd concentration 10^{17}–10^{18} cm^{-3} were Li-diffused as described elsewhere.[7] A wide range of undoped, Si-, and Sn-doped *n*-type GaAs starting materials with different electron concentrations were Li-doped in the same way. The diffusion conditions were chosen to ensure a Li concentration comparable to that of the shallow dopants and a homogeneous distribution through the bulk of the sample. A thin layer of about 50 μm was removed from the surface of the Li-diffused samples after which they were polished and chemically etched. The Li concentration profiles were analyzed by secondary-ion mass spectroscopy (SIMS) using a CAMECA IMS 4f system. A Li-implanted reference sample with known fluence was used for calibration. The carrier concentration and mobility were determined using the van der Pauw technique.

First we concentrate on acceptors in *p*-type GaAs material. Table I lists the hole concentration, hole mobility, and Li concentration of a few typical samples prepared by Li diffusion of two Zn-doped and a Cd-doped starting material at the indicated temperatures. The Li concentration is always comparable or smaller than the shallow acceptor concentration, except for sample 1*d*. For samples other than 1*d* the hole mobilities at room temperature and 77 K are higher in the Li-diffused samples than in the starting materials and the hole concentration smaller by a factor of 10^2–10^3. The mobility increase is largest in samples with high shallow-dopant concentration. The fact that the mobility increases when the hole concentration decreases, as demonstrated in the table, establishes that acceptor passivation has taken place. Both hole concentration and mobility can be restored to the initial values of the starting material by annealing the Li-diffused samples at 400–500 °C in pure Ga or Ar_2 atmosphere as shown in the table for samples 1*a*, 2*b*, and

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TABLE I. Effect of Li doping on the electrical properties of GaAs:Zn and GaAs:Cd.

Material, diffusion or annealing conditions		Li conc. (cm^{-3})	Hole conc. 300 K (cm^{-3})	Mobility 300 K ($cm^2/V s$)	Hole conc. 77 K (cm^{-3})	Mobility 77 K ($cm^2/V s$)
1	GaAs:Zn, as grown		4.0×10^{17}	220	1.6×10^{17}	330
1*a*	Li 400 °C, 8 h	4×10^{17}	1.0×10^{16}	260	3.9×10^{15}	930
	annealed 400 °C, 8 h in Ga		4.3×10^{17}	210	1.6×10^{17}	370
1*b*	Li 500 °C, 8 h	4×10^{17}	3.9×10^{15}	250	3.5×10^{15}	910
1*c*	Li 600 °C, 8 h		5.4×10^{15}	225	8.8×10^{14}	490
1*d*	Li 680 °C, 8 h	8×10^{17}	1.2×10^{15}	150	1.9×10^{14}	190
2	GaAs:Zn, as grown		1.3×10^{18}	160	1.3×10^{18}	120
2*a*	Li 500 °C, 10 h	1×10^{18}	7.5×10^{15}	245	1.1×10^{15}	555
2*b*	Li 600 °C, 10 h	9×10^{17}	8.9×10^{16}	190	2.3×10^{16}	580
	annealed 400 °C, 20 h in Ga	2×10^{16}	1.4×10^{18}	160	1.2×10^{18}	130
2*c*	Li 650 °C, 10 h	1×10^{18}	7.8×10^{15}	225	1.5×10^{15}	390
3	GaAs:Cd, as grown		7.5×10^{17}	180	3.6×10^{17}	185
3*a*	Li 500 °C, 10 h	7×10^{17}	5.5×10^{14}	205	7.5×10^{13}	435
3*b*	Li 600 °C, 10 h	1×10^{18}	1.8×10^{15}	210	1.7×10^{14}	390
	annealed 500 °C, 20 h in Ar_2	5×10^{15}	7.3×10^{17}	185	2.8×10^{17}	180
3*c*	Li 650 °C, 10 h	1×10^{18}	1.1×10^{15}	205	6.4×10^{13}	275

3*b*. Such annealing also reduces the Li concentration of the samples by about two orders of magnitude. Thus the passivation is concluded to be directly dependent to the presence of Li in the samples.

Figure 1 shows the temperature variation between 20 and 300 K of the hole mobility in as-grown, Li-diffused, and annealed samples made from a Zn-doped starting material ($p = 4\times10^{17}$ cm^{-3}) from Table I. Diffusions at 400–600 °C passivate the acceptors since the mobility increases in the entire temperature range while the hole concentration decreases. The largest increase of the mobility is observed between 50 and 100 K where the dominating carrier scattering mechanism is ionized impurity scattering. Hence, the increased hole mobility can be interpreted as a reduction of electrically active acceptors caused by the formation of neutral donor-acceptor complexes. The Li diffusion at 600 °C causes a smaller increase of the mobility than the ones at 400 and 500 °C but a similar decrease of the hole concentration. This is a clear sign of a simultaneous passivation and compensation. Li diffusion at 680 °C even reduces the hole mobility below the values of the starting material. The reduction suggests an increase of the number of ionized scattering centers in agreement with the high Li concentration measured in this sample. This is characteristic of samples diffused in the temperature range above ≈ 700 °C in which the hole concentration and mobility always decrease together for all starting materials. After annealing in pure gallium metal at 400 °C for 8 h the hole mobility of sample 1*a* is equal to that of the as-grown starting material within experimental accuracy at all temperatures as also illustrated in Fig. 1. The annealing also reestablishes the hole concentration of the starting material as listed in Table I. This is true for all Li-diffused *p*-type samples measured in the present investigation.

Figure 2 shows SIMS profiles of the Li concentration measured on the polished surfaces of two Li-diffused Cd- and Zn-doped samples before and after annealing the samples. The SIMS profiles in curves *a* and *b* show the Li concentration of samples 3*b* and 2*b*, respectively, after Li diffusion at 600 °C for 10 h. For both samples a homogeneous Li concentration similar to the shallow

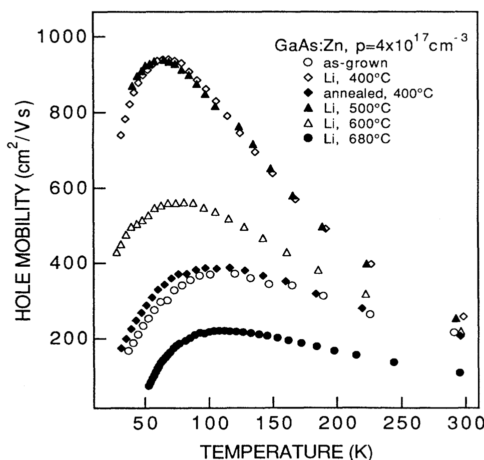

FIG. 1. Hall hole mobility as a function of temperature for the as-grown GaAs:Zn material 1 in Table I and five samples prepared as indicated in the figure. All diffusions and annealings lasted 8 h. Li concentration and hole concentration of all samples are listed in Table I.

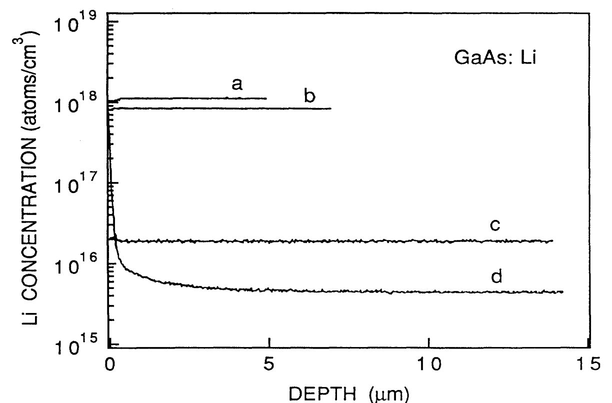

FIG. 2. SIMS profiles of the Li concentration vs depth of *p*-type bulk GaAs samples from Table I. *a*, GaAs:Cd, sample 3*b*; *b*, GaAs:Zn, sample 2*b*; *c*, same as *b* but annealed at 400 °C for 20 h in Ga; *d*, same as *a* but annealed at 500 °C for 20 h in Ar_2 atmosphere.

acceptor concentration is obtained through the bulk of the Li-diffused samples in agreement with earlier data.[7] The annealing of the samples causes out-diffusion of Li as already shown in Table I. If the samples are annealed in pure gallium metal, lithium diffuses out of the sample until a new equilibrium for the Li concentration of the Ga melt and the GaAs sample is established. The flat profile in curve *c* was obtained by annealing sample 2*b* at 400 °C for 20 h in Ga. When the annealing is performed in Ar_2 gas, Li accumulates on the surface instead. This is shown in curve *d* which was measured after annealing sample 3*b* at 500 °C for 20 h in Ar_2. In both cases the Li concentration after annealing is two orders of magnitude lower than its original value in the as-diffused samples. Annealing at higher temperatures further reduces the Li concentration.

Together, the Li diffusions at different temperatures which control the Li concentration of the samples and the annealing experiments that cause out-diffusion of Li from the samples show that the hole mobility and carrier concentration measured in Li-diffused *p*-type starting materials directly depend on the concentration of Li in the samples. A necessary condition for passivation of the shallow acceptors is that the Li concentration does not exceed the shallow-acceptor concentration significantly. Otherwise our results indicate the formation of randomly distributed Li-related donors that compensate the acceptors. At high Li concentrations the compensation dominates.

Li diffusion of *n*-type GaAs always reduces the electron concentration to a similar degree as found for the hole concentration of *p*-type samples under the diffusion conditions described above. However, careful investigation has not provided evidence for passivation of donors. Instead Li diffusion always causes the electron mobility to drop together with the electron concentration as expected for compensation. There is a further difference between Li-diffused *n*- and *p*-type GaAs. In a sharp contrast to the recovery demonstrated above for Li-diffused GaAs:Zn and GaAs:Cd, annealing at 400 °C has little effect on Li-diffused *n*-type samples. We now discuss the different configurations for Li in *n*- and *p*-type GaAs postulated in the literature in view of our results.

In Zn-doped GaAs hydrogen has been shown to diffuse to an As atom adjacent to the Zn acceptor and neutralize the configuration by bonding primarily to the As atom.[5,8] The hydrogen is suggested to be stable in a bond-centered configuration between the Zn_{Ga} acceptor and the As atom. The bond-centered position may not be as natural for the larger Li atom when it passivates acceptors in GaAs, however. In Si the Li atom occupies an interstitial lattice site when it pairs with the B acceptor[9,10] instead of the bond-centered Pankove configuration of hydrogen in the H-B pair.[11,12] This configuration agrees with the affinity of Li to the interstitial site in Si predicted from cluster calculations.[13] It seems fair to assume the same tendency for Li in GaAs.

Evidence from LVM spectroscopy of the Li-Cd pair in Li-diffused GaAs:Cd suggests that the Li atom sits on an interstitial lattice site with four As nearest neighbors in tetrahedral symmetry.[14] The interstitial Li donor passivates the substitutional acceptor by forming a neutral Li-Cd pair in GaAs with a $\langle 001 \rangle$ axis. Similar observations were made for the Mn and Mg acceptors.[14,15] In the case of Li-doped GaAs:Zn the vibrational spectrum is more complicated. This either suggests the existence of different nonequivalent Li-Zn configurations or complexes involving more than one Li atom.[14] The $\langle 111 \rangle$ orientation of the Li-B pair in Si and the $\langle 001 \rangle$ orientation of Li paired with the Cd, Mg, and Mn acceptors in GaAs are the simplest configurations of one Li atom passivating a shallow acceptor in a cubic lattice. Other possible complexes involve more than one Li atom and have lower symmetry.

The observation of Li-Zn and Li-Cd pairs in GaAs in local vibrational mode measurements[9,14] agrees with the passivation of Zn and Cd acceptors observed in this work. TEM studies of GaAs:Zn further support the evidence from LVM absorption that a large fraction of the Li introduced into the material is accommodated in Li-Zn pairs when the solubility of Li approximately equals the Zn concentration.[14,16] Higher Li concentrations are obtained by diffusion at higher temperatures after which a Li-related donor band appears in the LVM spectra.[16] The strength of the Li-Zn band in LVM absorption was found to decrease when the donor band increased.[16] These observations are in excellent agreement with our findings. As evident from Fig. 1 Li diffusions at 400 and 500 °C cause higher hole mobility. Table I shows that the Li concentration is comparable to the Zn concentration for these diffusion temperatures and neutral Li-Zn pairs that passivate the Zn acceptors are formed. After diffusion at 680 °C, on the other hand, the Li concentration exceeds the Zn concentration by a factor of 2 and the hole mobility decreases below that of the starting material. In this case the scattering of free holes by ionized impurities increases and we conclude that these Li-diffusion conditions produce Li-related donors which compensate the material.

The fact that local vibrational modes of Li paired with shallow donors have been observed in *n*-type starting materials[16] does not contradict the absence of passivation in such materials in our investigation. Isolated Li_{Ga} is expected to be a double acceptor and if paired with a single donor it still acts as a single acceptor. Such Li-related acceptors would be randomly distributed in the lattice acting as compensating centers, still giving rise to local vibrational modes of Li with donors. The conclusion we draw from our measurements is that Li-related acceptors predominantly cause the charge compensation observed in Li-diffused *n*-type samples. The observation that Li-diffused *n*-type starting material is resistant to annealing at 400 °C whereas Li-diffused *p*-type samples are restored by similar annealing as shown in Table I agrees with the above assumptions. Substitutional Li_{Ga}-related acceptors that compensate *n*-type materials can be expected to have higher dissociation energy than the Li_i-Zn and Li_i-Cd neutral complexes that passivate the Zn and Cd acceptors in *p*-type GaAs. In fact, the acceptor passivation reported here shows signs of instability close to the sample surface even at room temperature.

In summary, our detailed investigation of *p*-type

GaAs:Zn and GaAs:Cd gives measurements of Hall mobility and concentration which directly prove the passivation of shallow acceptors in GaAs through Li diffusion. The increase of hole mobility accompanying the reduced free hole concentration is attributed to the formation of neutral Li_i-Zn and Li_i-Cd defect complexes involving the interstitial Li donor. Evidence for the presence of such pairs has been provided by earlier LVM absorption measurements[14] although the orientation of the complexes in the lattice is uncertain. The preference observed in LVM absorption for Li-related donor complexes to be formed at higher diffusion temperatures at the cost of neutral pairs also supports the transition to conventional compensation of the p-type conductivity at higher temperatures reported here. As a contrast, we always observe conventional compensation of shallow donors in Li-doped n-type GaAs. The compensating acceptors are likely to involve the double Li_{Ga} acceptor paired with a single shallow donor, thus explaining the local vibrational modes of such pairs observed in LVM spectroscopy.

This research was partially supported by the Icelandic Council of Science and the University Research Fund.

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