Hydrogen passivation of shallow-acceptor impurities in *p*-type GaAs

N. M. Johnson, R. D. Burnham, R. A. Street, and R. L. Thornton
Xerox Palo Alto Research Center, Palo Alto, California 94304
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It is shown for the first time that hydrogen passivation of *p*-type GaAs produces electrical compensation of the shallow-acceptor impurity. This is demonstrated with capacitance-voltage and secondary-ion-mass spectrometry measurements on hydrogenated Zn-doped GaAs. In addition, it is shown that for comparable net dopant concentrations, passivation is far more extensive in *p*-type as compared to *n*-type GaAs; both metal-organic chemical-vapor-deposited (Zn and Se doped) and bulk GaAs (Zn and Si doped) were investigated. It is proposed that hydrogen passivation of Zn acceptors in GaAs involves interstitial diffusion of hydrogen to the vicinity of a zinc atom that is located at a gallium site. The hydrogen atom specifically bonds to an arsenic atom that is adjacent to the zinc. From the experimental results it is inferred that hydrogen passivation of shallow-acceptor impurities is a general physical phenomenon in semiconductors.

Hydrogen passivation of shallow-acceptor impurities has been extensively studied in single-crystal silicon. From electrical,[1–6] optical,[7,8] and compositional[8,9] measurements and theoretical calculations,[10,11] it has been established that hydrogen diffuses to the site of a substitutional shallow acceptor (e.g., boron) and bonds to a silicon nearest neighbor of the trivalent impurity, thereby neutralizing the acceptor center. In contrast, no change in electrical conductivity is observed after hydrogenating silicon doped with shallow-donor impurities.[1,2,4,5] Recently, it has been reported that hydrogen passivates the shallow-*donor* center in Si-doped *n*-type GaAs.[12] In this paper it is shown for the first time that hydrogen passivation of *p*-type GaAs produces electrical compensation of shallow-*acceptor* dopants. An immediate consequence of this finding is the inference that hydrogen passivation of shallow-acceptor impurities is a general physical phenomenon in both elemental and compound semiconductors.

Specimens of bulk single-crystal GaAs grown by the horizontal Bridgman technique and epitaxial layers of GaAs grown by metal-organic chemical-vapor deposition[13,14] (MOCVD) were exposed to monatomic hydrogen or deuterium from a gas discharge. The dopants in the starting materials are specified below in connection with the different measurements. Deuterium was used as a readily identifiable isotope of low natural abundance which duplicates the chemistry of hydrogen and is detectable with isotope separation and high sensitivity by secondary-ion-mass spectrometry (SIMS). The general features and operation of the hydrogenation system are described elsewhere.[9,15,16] A particular feature of the system used here, in contrast to that used in Ref. 12, is the placement of specimens on a hot stage that is located downstream from the plasma, with baffles for optical isolation. Therefore any possible effect on the passivation process from charged-particle bombardment or visible-uv illumination is minimized. The microwave plasma was operated at 70 W and at a pressure of 2 Torr, which consisted of 1.8 Torr of D_2 or H_2 and 0.2 Torr of O_2. The use of a partial pressure of oxygen in a hydrogen plasma is discussed in Ref. 9.

The application of SIMS for deuterium profiling is described elsewhere.[9,16] As applied to hydrogen passivation of shallow acceptors, the technique yields total concentrations of diffused deuterium and complements electrical measurements of acceptor compensation. The absolute concentration of deuterium, with approximately 50% accuracy, was determined from profiles of D that were implanted into GaAs to known fluences; the depth scales were established from the Cs-ion-sputtered crater depths, with the assumption of a constant sputtering rate, and are accurate to approximately 7%.

Depth profiles of the net dopant concentration were obtained from capacitance-voltage measurements on electrolytic Schottky-barrier diodes. These measurements were performed with a commercial instrument, the Polaron Semiconductor Profile Plotter. With this technique the semiconductor forms one electrode in an electrochemical cell, the differential capacitance of the Schottky barrier formed at the semiconductor-electrolyte interface yields the carrier concentration, and anodic dissolution provides a continuous depth profile of the concentration.[17] From profiles on bulk GaAs samples of known carrier concentrations (e.g. from Hall-effect measurements) and mechanical stylus measurements of crater depths, it was estimated that the absolute magnitude of the concentration is accurate to approximately 30% and the depth scales are accurate to approximately 15%.

The effect of deuterium passivation on Zn-doped GaAs is shown in Fig. 1. The material was grown by MOCVD at 800 °C with diethylzinc as the source gas for acceptor doping. Figure 1(a) shows the acceptor concentration in the epitaxial layer after different passivation conditions. An anneal in molecular deuterium at 300 °C for 30 min had no effect on the acceptor profile. However, annealing in monatomic deuterium at the same temperature strongly reduced the acceptor concentration to a depth of approxi-

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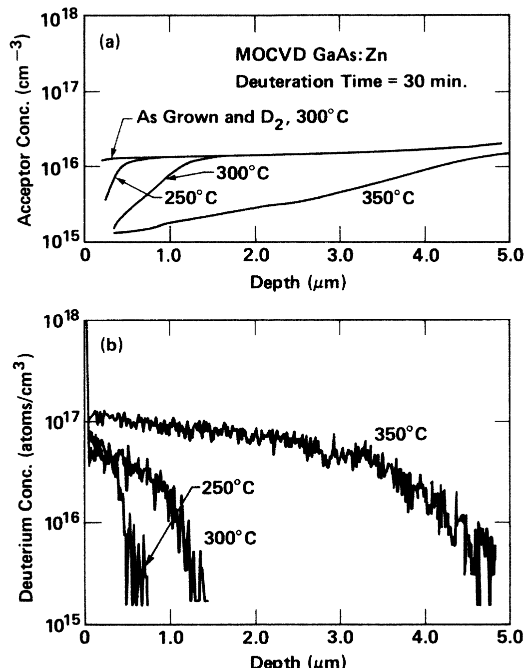

FIG. 1. Deuterium passivation in Zn-doped MOCVD GaAs. In (a) the acceptor concentration is shown for the epilayer as-grown, after an anneal in molecular deuterium (D_2, 300 °C, 30 min), and after deuterations at 250, 300, and 350 °C (for 30 min). In (b) depth profiles of deuterium after deuterations at 250, 300, and 350 °C for 30 min. are shown.

mately 1.4 μm, and the depth of compensation increased with deuteration temperature. Figure 1(b) shows the deuterium depth profiles for the anneal conditions of Fig. 1(a). The depth of deuterium penetration agrees closely with the depth of acceptor compensation. In related experiments, isothermal deuterations at 300 °C revealed an approximately $(\mathrm{time})^{1/2}$ dependence of the deuterium penetration depth, and the ratio of the depths of acceptor compensation for H versus D passivation equal within measurement accuracy the square root of the mass ratio. These observations are consistent with a diffusion-limited process, with H or D the diffusing species.

Depth profiles of deuterium in bulk GaAs are shown in Fig. 2. Specimens of p-type (Zn-doped), n-type (Si-doped), and semi-insulating (undoped) GaAs were deuterated at 300 °C for 30 min. In the n-type and semi-insulating samples, deuterium is not detectable beyond the immediate surface, whereas in the p-type material deuterium penetrates to greater than 5 μm. Thus, it appears that the diffusion coefficient for H is larger in p-type than in semi-insulating or n-type GaAs.

In agreement with Ref. 12, shallow-donor compensation was detectable in the near-surface region of n-type GaAs. This is illustrated in Fig. 3 for bulk GaAs doped with silicon to approximately 1×10^{17} cm^{-3}. After deuterating at 300 °C for 30 min, donor compensation extends to a depth of approximately 0.4 μm [Fig. 3(a)], and deuterium is detectable to this same depth [Fig. 3(b)]. Similar results were obtained with Se-doped n-type MOCVD GaAs. Since Si donors occupy sites on the Ga sublattice

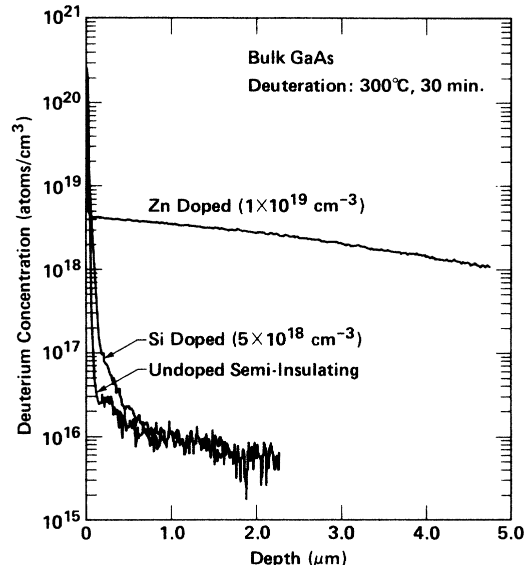

FIG. 2. Depth profiles of deuterium in bulk GaAs. Profiles are shown for deuterium diffusion at 300 °C for 30 min in p-type, n-type, and semi-insulating material.

while Se donors reside on the As sublattice, it appears that dopant passivation can proceed with donor impurities located on either sublattice of GaAs. In this connection it is of interest to note that the "$EL\,2$" complex in GaAs is a deep donor that can be hydrogenated and is generally considered to involve the $\mathrm{As_{Ga}}$ antisite defect.[18,19]

To further illustrate hydrogen diffusion in p-type GaAs, deuterium profiles are shown in Fig. 4 for a set of isochronal (30 min) deuterations. The material was bulk GaAs doped with zinc to a concentration of approximately 1×10^{19}cm^{-3}. At 200 °C the deuterium profile superimposes on the uniform zinc concentration to a depth of approximately 0.8 μm. Similar behavior has been documented for D passivation in boron-doped silicon.[9] At 250 °C and above, the D profile deviates from the zinc concentration and extends deep into the GaAs substrate. Acceptor compensation was detected with $C-V$ measure-

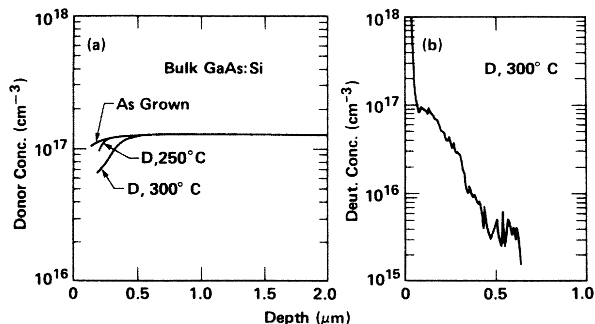

FIG. 3. Deuterium passivation in Si-doped bulk GaAs. In (a) the donor concentration is shown for the as-grown material and after deuterations at 250 and 300 °C for 30 min. In (b) the deuterium depth profile after deuteration at 300 °C for 30 min is shown.

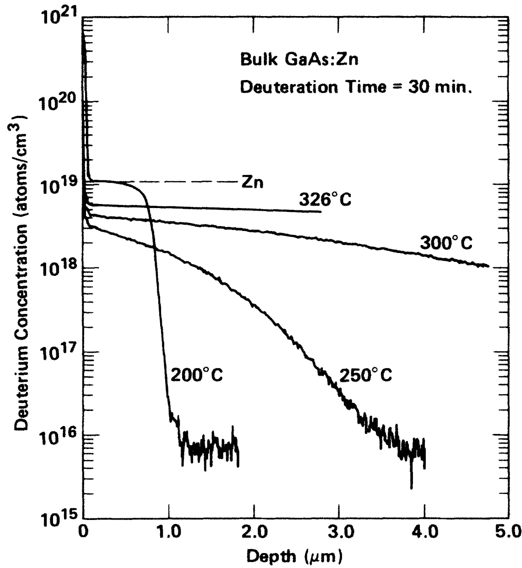

FIG. 4. Deuterium profiles in p-type GaAs for isochronal (30 min) deuterations. Also shown is the Zn concentration.

ments, although these were less reliable at degenerate dopant concentrations. The deviation of the D profile from the zinc concentration above 200 °C may be ascribed to the onset of thermal dissociation of the compensating center. Finally, hydrogen passivation of shallow acceptors was also detected in Zn-diffused bulk semi-insulating GaAs.

The experimental results presented in this paper yield the following observations: (1) shallow-acceptor impurities are compensated by exposing p-type (e.g., Zn-doped) GaAs to monatomic hydrogen (Fig. 1), (2) the depths of hydrogen (deuterium) penetration and dopant compensation are equal within experimental accuracy (Fig. 1), (3) hydrogen penetrates to a comparable depth in semi-insulating and n-type material (Fig. 2), (4) under comparable conditions hydrogen passivation of dopants extends to a greater depth in p-type as compared to n-type GaAs (Figs. 1–3), and (5) the hydrogen diffusion profile is strongly influenced by the zinc concentration (Figs. 1 and 4). While shallow-donor[12] and deep-donor[18] compensation in GaAs have been previously reported, the results presented here establish for the first time hydrogen passivation of a shallow-*acceptor* dopant in a compound semiconductor.

In n-type silicon it has recently been demonstrated with combined conductivity and Hall measurements that hydrogen passivates shallow-donor impurities (e.g., P).[20] Furthermore, it was predicted from total-energy calculations that donor passivation in n-type Si results from placing H in an antibonding position of either a substitutional P atom or a Si atom that is adjacent to the P atom. A similar chemical-bonding configuration may be responsible for donor passivation in n-type GaAs.

It is proposed here that hydrogen passivation of shallow-acceptor impurities in p-type GaAs involves a mechanism similar to that which has recently been identified for shallow acceptors in silicon.[8,21] Namely, hydrogen diffuses interstitially to the vicinity of a zinc atom that is located at a substitutional site on the gallium sublattice, Zn_{Ga}. The hydrogen atom specifically bonds to an arsenic atom that is adjacent to the zinc, and the zinc atom threefold coordinates with the remaining arsenic nearest neighbors. The overall chemical reaction for this neutralization process would be as follows:

$$Zn_{Ga}{}^{-} + h^{+} + H^{0} \rightarrow (Zn_{Ga}H)^{0} , \quad (1)$$

where h^{+} is a free hole, H^{0} is a neutral hydrogen atom, and $(Zn_{Ga}H)^{0}$ is a neutral Zn-H pair. We are currently seeking spectroscopic evidence for the above model. Theoretical examination of Eq. (1) would also be desirable. However, the experimental results presented here demonstrate that hydrogen passivation of shallow-acceptor impurities occurs in compound as well as elemental semiconductors.

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