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Effect of hydrogenation on defect levels in bulk n-GaAs

T. W. KANG, I. H. BAI, C. Y. HONG, C. K. CHUNG
Department of Physics, Dongguk University, 3-26 Chungku Pildong Seoul 100-715, Korea
T. W. KIM*
Department of Physics, Kwangwoon University, 447-1 Wolgye-Dong Nowon-Ku Seoul 139-050, Korea.

The hydrogenation effects on the defect levels existing in bulk n-GaAs were investigated by deep-level transient spectroscopy and photoluminescence. The three electron traps of the GaAs bulk samples were observed, and their activation energies were $E_c - 0.35$ eV (E1), 0.56 eV (E2), and 0.81 eV (E3). After hydrogenation at 250 °C for 3 h, the electron trap at $E_c - 0.35$ eV was almost completely passivated and a new trap (EN1) at $E_c - 0.43$ eV was observed. As a result of furnace annealing for 5 min at 300 °C, the EN1 trap disappeared, and the E3 trap passivated by hydrogenation reappeared. In particular, the trap E1 recovered to 90%. The photoluminescence measurements of the hydrogenated samples show that the germanium-related peak was passivated, and the intensity of the dominant bound exciton peak increased remarkably. After a thermal annealing for 15 min at 300 °C, the original intensity of the germanium-related peak was restored.

1. Introduction

The effects of hydrogen atoms in semiconductors have been investigated in relation to electrical transport and optical studies for many years [1–3]. The hydrogen atoms in GaAs samples passivate the impurities due to the formation of neutral complexes with the dopant atoms, and the concentration in the deep level can be decreased by passivation of dangling and defective bonds [3–5]. Thus, hydrogen atoms have an effect on the reduction of bad properties and the improvement of device performance in semiconductors [6–8]. In addition, passivated defect levels may be recovered by hydrogenation, as shown by studies using mainly deep-level transient spectroscopy (DLTS) measurements [9–11].

In this study, the effect of hydrogenation on the defect levels in n-GaAs (1 0 0) samples and the variation of the defect levels by thermal treatment between 300 and 600 °C have been investigated by DLTS and photoluminescence (PL) measurements.

2. Experimental procedure

The sample used in this experiment was undoped GaAs (1 0 0) grown by the horizontal Bridgman (HB) method, and its carrier concentration was 1.5×10^{16} cm^{-3}. The GaAs wafers were etched in a mixture of NH_4OH, H_2O_2, and H_2O (1:1:10) for 1 min and hydrogenated by an r.f. plasma system. The hydrogenation conditions are listed in Table I. To investigate the effect of thermal treatment for hydrogenated samples, the samples were treated by using a furnace annealing system between 300 and 600 °C in a nitrogen atmosphere for approximately 5 min.

TABLE I Hydrogenation conditions

Parameters	Conditions
Substrate temp. (°C)	250
Hydrogen pressure (atm)	2/3
Power density (W cm^{-2})	3
Time (h)	3

DLTS and PL measurements were carried out in order to investigate the passivation for the impurity levels of the hydrogenated GaAs samples. Schottky diodes were established by evaporating gold through a mask, resulting in a contact area of 0.5 mm^2 gold dots: and the back of the contacts to the samples were fabricated by Au–Ge evaporation and annealed at 450 °C for 1 min. The DLTS measurements were performed using a cryostat in which the temperature of the samples was varied from 77–450 K. For the PL measurements, the samples were kept at 5 K using a helium refrigerator, and an argon ion laser with a wavelength of 514.5 nm and a power of 30 mW was used.

3. Results and discussion

The results of *C–V* measurements on undoped HB GaAs before hydrogenation are shown in Fig. 1. The carrier concentrations of the samples were distributed uniformly to 2 μm deep in the GaAs layers, and the

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* Author to whom all correspondence should be addressed.

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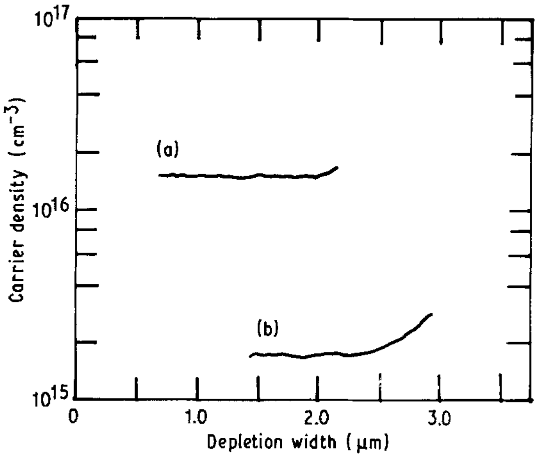

Figure 1 *C–V* depth profile of undoped GaAs (a) before, (b) after hydrogenation.

carrier concentration was about $1.5 \times 10^{16}\,cm^{-3}$. However, the *C–V* results for hydrogenated GaAs annealed at 250 °C for 3 h showed that the carrier concentration was $1.7 \times 10^{15}\,cm^{-3}$ at 1.4 μm, and the concentration increased greatly with depth, in comparison with that of undoped HB GaAs. This decrease in the carrier concentration by hydrogenation occurred over a distance of 3 μm from the sample surface; this consequence depends on substrate temperatures and hydrogenation times [9, 12].

The results of DLTS measurements on GaAs wafers before and after hydrogenation are shown in Fig. 2. DLTS spectra with a rate window of $8\,s^{-1}$ under a reverse bias voltage of − 3 V, and an amplitude of 3 V with a 1 ms pulse width are shown. Only three deep traps, i.e. E1, E2 and E3, appear in the undoped GaAs as shown in Fig. 2. These traps appear typically at the electron traps in bulk GaAs, corresponding to the commonly mentioned EL2, EL3 and EL6 levels mentioned [13]. However, when the samples were hydrogenated at 250 °C for 3 h, the E1 and E3 traps, but not the E2 trap, showed the passivation phenomena. In particular, while the E3 trap passivated almost completely, a new trap appeared at 187 K, and the new trap was indicated by the EN1 level. Thus, the passivation of the existing traps by hydrogenation appears to be due to the neutralization of activation for the existing traps by a hydrogen atom [1, 14], and the increase of the concentration in the E2 trap by hydrogenation is induced due to surface damage resulting from a hydrogen plasma process; the creation of the new EN1 trap originates from the interaction between a hydrogen atom and existing deep levels [15].

To investigate the thermal effects of hydrogenated samples, the samples were annealed in a nitrogen atmosphere for 5 min using a furnace annealing system at 300, 400, 500 and 600 °C. The results of DLTS measurements on the samples are shown in Fig. 3, in which the trap created by hydrogenation is seen to disappear, and at the same time, a passivated E3 trap level reappears on the samples annealed at 300 °C. Thus, the annihilation of the EN1 trap level and the recovery of the existing traps are considered to be due to the out-diffusion of hydrogen atoms in GaAs, and about 90% of the E1 trap was recovered at that temperature. As the thermal treatment temperature increases, the concentration variation in the E1 trap increases rapidly in comparison with that of other traps. A new trap for the samples annealed at 500 °C appears at 115 K, and this trap is indicated by the E4 level.

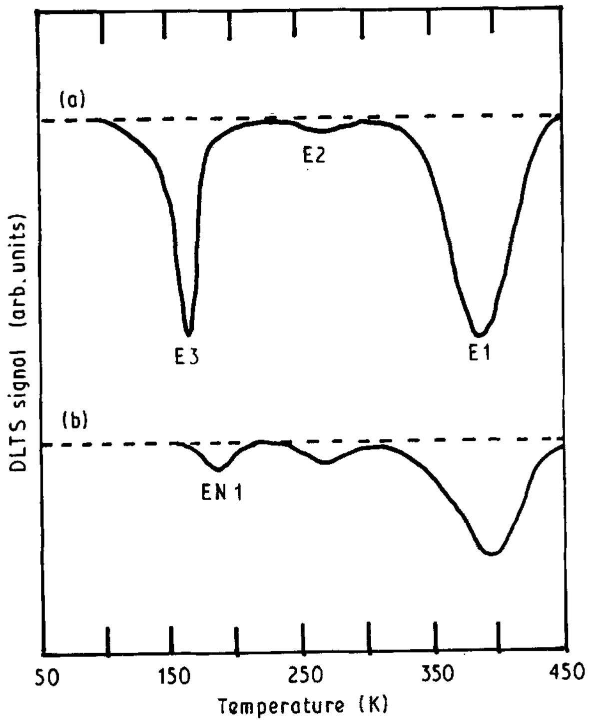

Figure 2 DLTS spectra of electron traps before and after hydrogenation for undoped GaAs (a) before, (b) after hydrogenation.

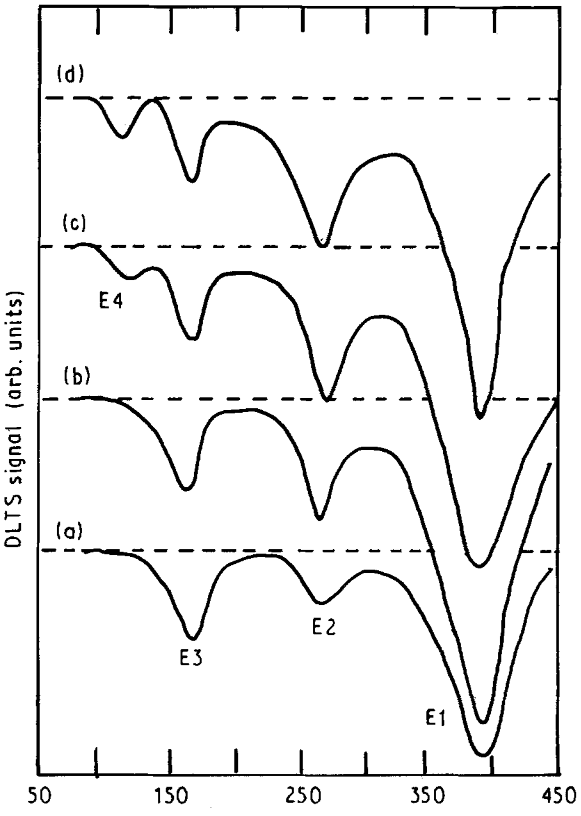

Figure 3 DLTS spectra of hydrogenated GaAs samples after furnace annealing for 5 min at different temperatures (a) 300 °C, (b) 400 °C, (c) 500 °C, (d) 600 °C.

The Arrhenius plots for the electron traps observed in Figs 2 and 4 are shown in Fig. 4, and the activation energies and the capture cross-sections obtained from the slopes and intersections of the straight lines are summarized in Table II. As shown in Table II, the activation energy ($E_c - 0.17$ eV) of the E4 level is smaller than that of EL9 ($E_c - 0.22$ eV), and the origin of the level corresponds to the EL10 level of the V_{Ga}–V_{As} defect complex existing in bulk GaAs [16].

The PL spectra for bulk GaAs and hydrogenated GaAs at 5 K are shown in Fig. 5. The peaks at 1.512, 1.493, 1.417 and 1.458 eV appear in the PL spectra of bulk GaAs. The peaks at 1.512 and 1.493 eV are the same as those in GaAs PL spectra, typically due to the bound exciton (A°, X) in the carbon acceptor and the recombination between a free electron and a bound hole in the carbon acceptor, where carbon is a residual impurity [8, 17]. The peaks at 1.417 and 1.458 eV are the first phonon replicas of the $(e\,A^\circ)_{Ge}$ and $(e\,A^\circ)_C$ luminescences generated by the recombination between a free electron and a hole bound in a Ge acceptor. When the samples were hydrogenated at 250 °C for 3 h, the peak at 1.471 eV related to germanium became passivated. In this case, while the intensity of the peak (A° X) increased considerably, the full-width at half maximum decreased to 6.47 meV in comparison with that of bulk GaAs. This behaviour results from the passivation of a nonradiative deep trap by hydrogen atoms [8, 10].

The PL spectra, dependent on thermal treatment temperatures, for samples hydrogenated for 5 min, are shown in Fig. 6. When the samples were annealed at 300 °C, the passivated peak of 1.471 eV reappeared. However, when the samples were annealed at 600 °C, the peak was annihilated completely. Thus, after thermal treatment, the creation of the 1.471 eV peak is considered to be due to the out-diffusion of hydrogen atoms from the samples; the annihilation of the peak at 600 °C is due to the emission of a hole bound in a neutral acceptor (C°_{As}). As the treatment temperature increases, the intensities of the luminescence peaks decrease gradually. This trend originates from the diminution of the crystallinity due to thermal damage.

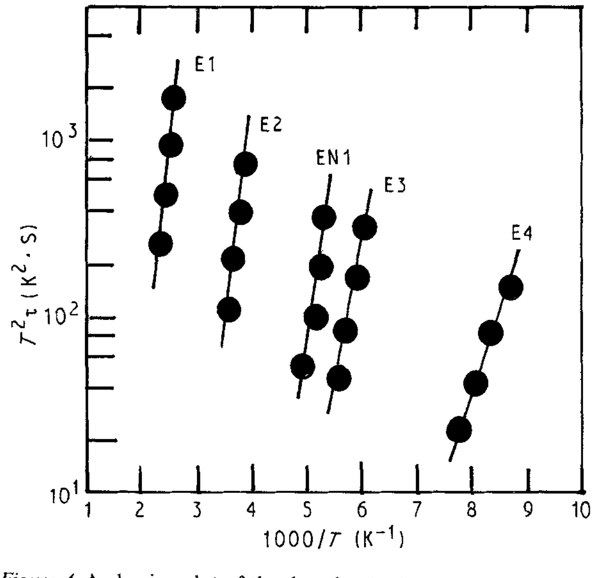

Figure 4 Arrhenius plot of the deep levels shown in Figs 2 and 3.

TABLE II Summary of deep-level parameters in undoped HB GaAs

Trap	Activation energy (eV)	Capture cross-section (cm^2)	Commonly used trap level
E1	0.81	8.32×10^{-14}	EL2
E2	0.56	1.98×10^{-13}	EL3
EN1	0.43	4.79×10^{-12}	
E3	0.35	6.27×10^{-13}	EL6
E4	0.17	4.95×10^{-16}	EL10

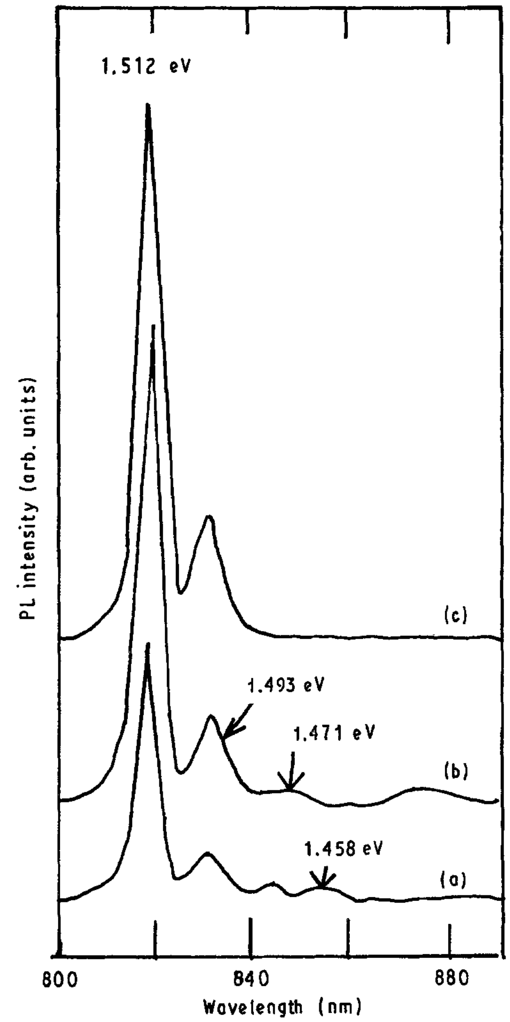

Figure 5 PL spectra for an undoped GaAs sample: (a) before hydrogenation, (b) after hydrogenation at 250 °C for 3 hours and (c) annealing at 600 °C.

4. Conclusion

At a passivation depth of 1.4 μm in hydrogenated bulk n-GaAs, DLTS measurements have shown the creation of the trap EN1 ($E_c - 0.43$ eV) and the passivation of the E1 ($E_c - 0.81$ eV) and the E3 ($E_c - 0.35$ eV) traps. In particular, when the samples were annealed to 600 °C, the E3 level became almost completely passivated, the new EN1 trap disappeared, and the passivated E3 trap reappeared at 300 °C. The E1 trap was recovered to 90% at that temperature. A E4 trap ($E_c - 0.17$ eV) appeared at 500 °C, and its origin corresponds to the EL10 level of the V_{Ga}–V_{As} defect complex. The results of PL measurements demonstrated that the samples hydrogenated at 250 °C for

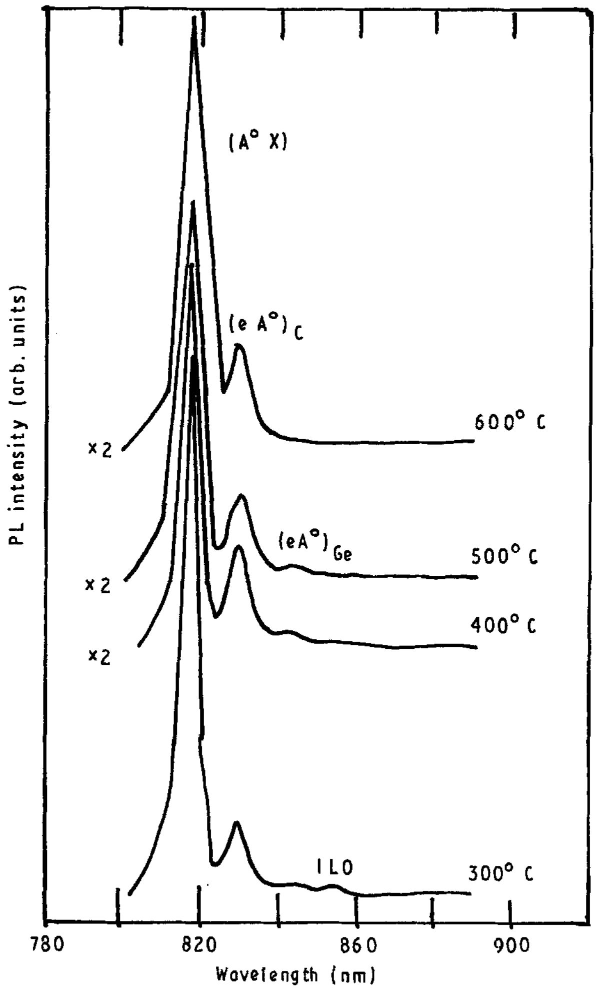

Figure 6 PL spectra of a hydrogenated GaAs sample after furnace annealing at 300, 400, 500 and 600 °C for 5 min.

3 h showed passivation of the 1.471 eV peak related to germanium. In this case, the intensity of the peak (A° X) increased remarkably; this phenomenon is due to the passivation of a nonradiative deep trap by hydrogen atoms. When the samples were annealed at 300 °C, the passivated peak reappeared. The recovery of the peak is regarded to be due to out-diffusion of hydrogen atoms from the samples.

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