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Hydrogen-related metastable defects in passivated n-type GaAs grown by metal-organic vapor-phase epitaxy

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Undoped n-type GaAs grown by metal-organic vapor-phase epitaxy is exposed to a hydrogen or a deuterium plasma. Two dominant deep levels, having energies $E_c - 0.2$ eV and $E_c - 0.57$ eV, are formed after hydrogenation. Their depths into the material correspond directly with the depth to which the shallow donors have been passivated. Furthermore, isothermal annealing measurements under zero- and reverse-bias conditions reveal that the two levels are metastable. The transformations from one configuration to the other obey first-order kinetics, with the following transformation rates: $\nu_1(T) = 1.2 \times 10^8 \exp[(-0.82 \text{ eV})/kT]$ and $\nu_2(T) = 8.0 \times 10^{10} \exp[(-0.95 \text{ eV})/kT]$. We attribute the deep levels to the formation of a hydrogen-related complex. The new hydrogen complex is found to be more stable than the shallow donor-hydrogen complex.

Defect states with metastable properties have in recent years been studied in several III-V compounds.[1-5] Two metastable defects, labeled $M3$ and $M4$, were recently measured by Buchwald and co-workers[4,5] in GaAs grown by metal-organic vapor-phase epitaxy (MOVPE). The fact that other groups have not detected these defects in MOVPE-grown GaAs of similar specifications[6-8] makes an investigation into the possible origin of these defects a matter of importance. Tabata, Pudensi, and Machado[9] subsequently found that the presence of these metastable defects was related to the V-to-III ratio used during the MOVPE growth. Based on these results they suggested that the metastable defects may originate from As interstitials, which would predominate at high V-to-III ratios.

During the course of our studies on the hydrogen passivation of GaAs,[10,11] we have investigated the effect of the hydrogen plasma on the deep levels in the material. Early deep-level transient spectroscopy (DLTS) studies[12,13] had shown that the concentration of most deep levels present in GaAs could be considerably reduced, in some cases to below detection limits, through the passivation by hydrogen. On the other hand, Cho *et al.*[14] reported the creation of new deep levels in undoped horizontal Bridgman (HB) -grown GaAs, after exposure to a hydrogen plasma. Detailed analysis of the newly created levels was difficult, however, due to the overlapping of the new levels with the deep levels present in the unpassivated material. In another DLTS study of HB GaAs passivated under different plasma power densities, Jalil *et al.*[15] also demonstrated the creation of new deep levels after hydrogenation.

In this paper we show that the two metastable deep levels reported by Buchwald and co-workers[4,5] can be formed in MOVPE-grown GaAs by exposure to a hydrogen plasma. The fact that hydrogen is responsible for their presence is further supported by annealing measurements under reverse-bias conditions, which show the drift of hydrogen deeper in the material with an accompanied increase in the concentration of the metastable defect.

The GaAs material used in this work consisted of a 10-μm-thick undoped layer, grown at 670 °C by MOVPE on a Si-doped ($n = 1 \times 10^{18}$ cm^{-3}) GaAs substrate. A V-to-III ratio of 40 was used in the growth, in order to ensure that the carrier concentration was in the low 10^{15}-cm^{-3} range. Further details of the growth conditions have been given previously.[8] After forming AuGe-Ni Ohmic contacts on the back of the substrate, the GaAs was exposed for 2 h at 180 °C to either a hydrogen or a deuterium plasma in a remote dc system.[16] These conditions were sufficient to passivate the donor impurities to a depth ~ 1.7 μm into the material. The atomic hydrogen forms a complex with the ionized donor impurities, rendering them electrically neutral.

The surface of the GaAs after plasma treatment showed no visible signs of degradation. After rinsing the GaAs in acetone and treating in HCl:H_2O (1:1) for 1 min, semitransparent Schottky contacts were formed on the plasma-exposed surfaces by evaporating Au dots ($\sim$ 30

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nm thickness, 1 mm diameter) through a metal mask. Some Schottky diodes were also fabricated on a reference sample that had not been exposed to the plasma. Standard capacitance-voltage (C-V) measurements at 1 MHz were used to profile the 300-K carrier concentration in the GaAs. DLTS measurements were carried out within the temperature range 77–440 K, using a lock-in amplifier based system.

Figure 1 shows the DLTS spectra measured in the passivated and nonpassivated GaAs samples. In each case the conditions of measurement were identical, namely, a filling pulse $V_p = 2$ V superimposed on a constant reverse bias $V_r = 2$ V. It is seen from curve (a) that one electron trap (having a concentration 2×10^{14} cm^{-3} and an activation energy 0.82 eV) dominates the deep-level spectrum of the as-grown GaAs. By comparison with the literature, it is identified as the well-known $EL2$ deep level,[17] occurring in bulk-grown as well as MOVPE- and VPE-grown GaAs. Apart from the $EL2$ level, no other electron traps were detected in the as-grown GaAs, within the resolution of the system ($\sim 10^{11}$ cm^{-3}).

Curve (b) of Fig. 1 shows the effect of the hydrogenation on the deep levels. The $EL2$ has been considerably reduced through passivation, in agreement with the work of Lagowski *et al.*[18] The slight shift of the DLTS peak towards higher temperatures after passivation is presently not understood. The main features of curve (b), however, are the emergence of two new deep levels, occurring at 174 and 313 K. These two levels will be shown to have the same characteristics as the two levels reported before by Buchwald and co-workers,[4,5] who measured them in as-grown (MOVPE) Si-doped GaAs. Using their notation, therefore, we shall refer to the two levels as $M3$ and $M4$. The fact that we only measure levels $M3$ and $M4$ *after* passivation is the first indication that hydrogen is in some way responsible for their presence.

In curve (c) of Fig. 1, the DLTS spectrum from the deuterated GaAs shows a similar trend to the hydrogenated sample. It is noted, however, that while the maximum of level $M4$ occurs at the same temperature in both cases, there is a significant shift of level $M3$ to a higher temperature (321 K) for the deuterated sample. As was noted by Buchwald and co-workers,[4,5] level $M3$ shows a strong Poole-Frenkel effect. To minimize this influence on the measured activation energy, therefore, the reverse bias was set at $V_r = 1$ V, upon which was superimposed $V_p = 1$ V. Our measured activation energy (0.57 eV) for level $M3$ is smaller than the value of 0.61 eV reported by Buchwald and co-workers.[4,5] The measured activation energy of 0.32 eV for level $M4$, on the other hand, showed no field dependency.

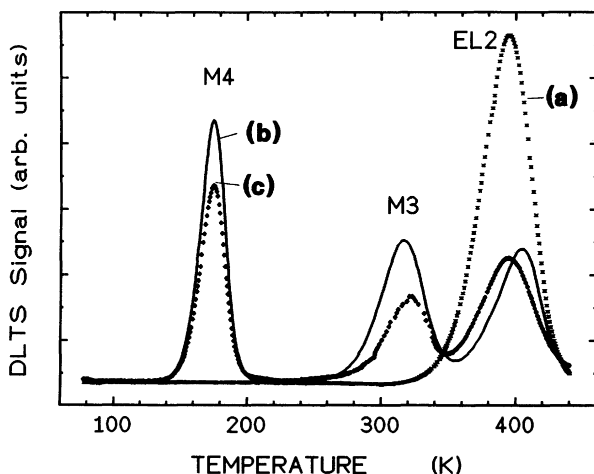

FIG. 1. DLTS spectra measured under identical conditions in undoped n-type MOVPE-grown GaAs: (a) as-grown; (b) after passivation in a hydrogen plasma; and (c) after passivation in a deuterium plasma. The emission rate is 100 s^{-1}.

The metastable properties of levels $M3$ and $M4$ are clearly evidenced in the following manner: By annealing under zero-bias (open circuit) conditions at 400 K for 10 min, the concentration of the level $M3$ reaches a maximum, with level $M4$ completely disappearing. A similar anneal at 400 K under reverse bias has the opposite effect. Thus the defect changes configuration by application of an electric field at elevated temperatures. Furthermore, this transformation is completely reversible, simply by annealing at 400 K, either with or without bias.

From a series of isochronal anneals within the temperature range 320–410 K, Buchwald and co-workers[4,5] determined the energies of transformation for the two configurations to be 0.8 eV (for $M4 \rightarrow M3$) and 1.7 eV (for $M3 \rightarrow M4$). In their calculations, they implicitly assumed that the transformations obeyed first-order kinetics, although this was not experimentally verified. Furthermore, the transformation $M3 \rightarrow M4$ yielded an unusually high preexponential factor of 10^{21} s^{-1}. We have carried out isothermal anneals under specific bias conditions, at temperatures within the range $315 \leq T \leq 380$ K to study the kinetics governing the transformations. The transformation $M4 \rightarrow M3$ was investigated by the following procedure: The Schottky diode was initially annealed at 400 K for 10 min while under reverse bias, in order to maximize $M4$. Thereafter it was cooled to a specific temperature T, while still under reverse bias, before beginning a zero-bias anneal at T. After an annealing time t, the annealing process was terminated by rapidly cooling the sample holder to 150 K (using liquid nitrogen). From the resulting DLTS scan, the amplitude of the $M4$ level, $N(t,T)$, was measured. The process was then repeated for longer annealing times, from which the rate of decay of $M4$ at a temperature T could be evaluated.

Figure 2 (right-hand axis) shows the results obtained from the annealing sequence at 340 K. The linear dependency proves that the transformation process between the two configurations ($M4 \rightarrow M3$) obeys first-order kinetics for all annealing times and satisfies

$$N(t,T) = N_0 \exp[-\nu_1(T)t], \tag{1}$$

where N_0 is the maximum amplitude of level $M4$ and $\nu_1(T)$ is the transformation rate. Similarly, isochronal anneals at 325, 360, and 380 K yielded equally good straight lines, from which $\nu_1(T)$ for each annealing tem-

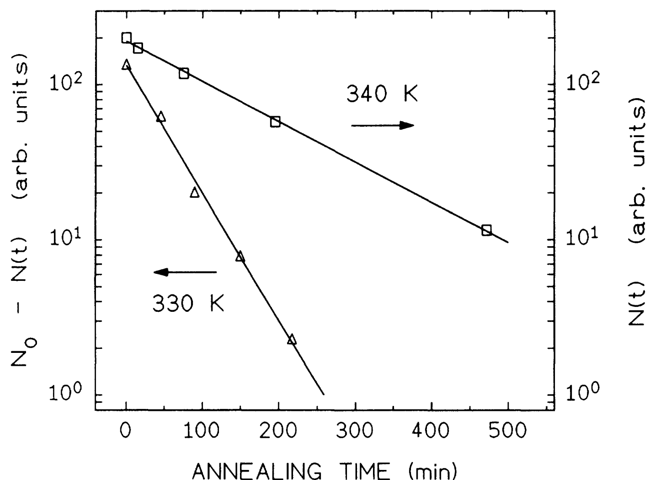

FIG. 2. Analysis of the annealing kinetics based on Eq. (1) (□, right-hand scale) and Eq. (2) (△, left-hand scale) for the transformation $M4 \rightarrow M3$ (at 340 K) and $M3 \rightarrow M4$ (at 330 K), respectively.

perature could be obtained.

Following a similar procedure, the transformation $M3 \rightarrow M4$ was studied by measuring the formation of $M4$ as a function of zero-bias annealing time t, for specific temperatures within the range $315 \leq T \leq 370$ K. Figure 2 (left-hand axis) shows the results from just one annealing temperature (330 K), which satisfies the equation

$$N(t,T) = N_0(1 - \exp[-\nu_2 t]). \quad (2)$$

The fact that both transformations obey first-order kinetics is further proof that levels $M3$ and $M4$ are indeed metastable configurations of the same defect. From the measured $\nu(T)$, we obtain the Arrhenius plots seen in Fig. 3, which yield $\nu_1(T) = 1.2 \times 10^8 \exp[(-0.82\text{ eV})/kT]$ for $M4 \rightarrow M3$ and $\nu_2(T) = 8.0 \times 10^{10} \exp[(-0.95\text{ eV})/kT]$ for $M3 \rightarrow M4$. Our measured energy of 0.82 eV for the transformation $M4 \rightarrow M3$ compares well with the value of 0.8 eV reported by Buchwald and coworkers.[4,5] We do, however, find both a significantly smaller energy (0.95 eV) and a significantly smaller exponential prefactor (8.0×10^{10} s^{-1}) for the transformation $M3 \rightarrow M4$ compared with the respective values of 1.7 eV and 10^{21} s^{-1} measured by Buchwald and co-workers. We attribute this discrepancy to the fact that we used isothermal anneals, which are expected to yield more appropiate expressions for the transformations, compared with isochronal anneals.

From the results presented thus far, we conclude that the levels $M3$ and $M4$ are two configurations of the same metastable defect. The stability of the defect was examined as follows: First, by annealing in the open-circuit configuration at 373 K for 2 h under illumination (using the emission from a $Al_xGa_{1-x}As$ power laser diode focused onto the semitransparent Schottky contact), it was possible to completely reactivate the shallow donors in agreement with previous work.[11] DLTS measurements however, showed no change in the concentration of levels $M3$ and $M4$ after reactivation of the shallow donors. We conclude, therefore, that the defect responsible for levels $M3$ and $M4$ is more stable than the donor-hydrogen complex.

Second, the stability of the defect was examined by annealing in the dark at $T > 453$ K under reverse-bias conditions. Annealing at both 453 and 473 K with a reverse bias $V_r = 3$ V applied to the Schottky diode, resulted in the concentration of $M4$ decreasing in the region $x < 1.3$ μm, and increasing at $x > 1.3$ μm. After each anneal, the temperature was reduced to 400 K for 10 min, during which time a reverse bias $V_r = 10$ V was applied (in order to maximize the amplitude of $M4$ for the entire profiling depth). The carrier concentration profile, measured before and after the same reverse-bias anneal at 453 K, shows a reactivation of the donors in the region $x < 1.3$ μm, coupled with the simultaneous increase in passivation in the region $x > 1.3$ μm can be explained in terms of the field-assisted drift of the thermally dissociated H^-, towards the edge of the space-charge region.

The $M4$ deep level shows a similar (although much slower) trend and may therefore be explained in a similar manner: We assume that the defect responsible for levels $M3$ and $M4$ is some complex, XH, between hydrogen and a defect X either present in the material before passivation, or formed during the passivation treatment. Surprisingly, the $M3$ level is very close to the oxygen level, recently detected in GaAs.[19] Further studies will clarify the correlation between these two defects. Annealing at elevated temperatures results in the partial dissociation of the XH complex, according to $XH \rightleftharpoons X^+ + H^-$. We assume that the diffusivity of the defect X is very low at the annealing temperature. The electric field drifts the thermally dissociated hydrogen towards the edge of the space-charge region, where new XH complexes are formed, thus leading to an increase in the measured $M4$ concentration within the region $x > 1$ μm.

The fact that temperatures as high as 453 K are required to dissociate the XH complex implies that the

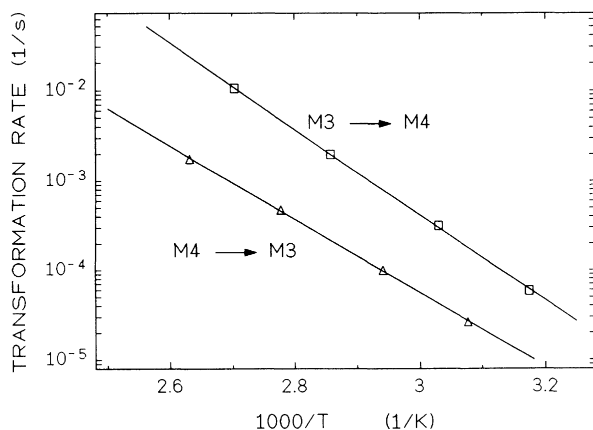

FIG. 3. Arrhenius plot of the transformation rates.

transformations $M3 \rightleftharpoons M4$, which were measured within the range $315 \leq T \leq 380$ K, do not involve the actual dissociation of the H from the XH complex. Rather, it is likely that the transformations may be attributed to changes in the actual configuration of the complex.

Tabata, Pudensi, and Machado[9] suggest that interstitial As could be involved in the metastable defect, as this would explain the observed influence of the V-to-III ratio on the concentration of the metastable levels. It is also true, however, that an increase in the V-to-III ratio during growth implies an increase in the concentration of H in the MOVPE reactor (if one adheres to the normal procedure of varying the group-V source while keeping the group-III source constant).

Very recently, Cho *et al.*[20,21] reported metastable behavior of deep levels in hydrogenated melt-grown (HB) Si-doped GaAs, of concentration $n = 1.2 \times 10^{17}$ cm^{-3}. They measured metastability occurring between a level $H2$ (having similar characteristics to our $M3$) and a native defect, $H3$, which was present in their as-grown material. Although they also detect a level $H4$ (most likely our $M4$), they assume this to be an "electric field induced defect," exhibiting no metastability. By comparison, the epitaxially grown GaAs used in this work contained no $H3$ defect, either before or after hydrogenation. The metastability we have studied clearly occurs between the levels $M3$ and $M4$.

To conclude, we have presented evidence to show that hydrogen is responsible for the metastable levels reported by Buchwald and co-workers.[4,5] The hydrogen can be incorporated in the GaAs during the MOVPE growth process. This may have important implications when considering the growth of device structures by MOVPE. We have also shown that the transformation between the two metastable configurations obeys first-order kinetics throughout the entire annealing cycle. From these measurements the transformation rates were determined. Finally, the stability of the metastable defect has been found to be greater than that of the shallow donor-hydrogen complex.

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[1] M. Levinson, J.L. Benton, and L.C. Kimerling, Phys. Rev. B **27**, 6216 (1983).

[2] A. Chantre, A. Vincent, and D. Bois, Phys. Rev. B **23**, 5335 (1981).

[3] D.V. Lang, in *Deep Centres in Semiconductors*, edited by S.T. Pantelides (Gordon and Breach, New York, 1986), Chap. 7, p. 489.

[4] W.R. Buchwald, N.M. Johnson, and L.P. Trombetta, Appl. Phys. Lett. **50**, 1007 (1987).

[5] W.R. Buchwald, G.J. Gerardi, E.H. Poindexter, N.M. Johnson, H.G. Grimmeiss, and D.J. Keeble, Phys. Rev. B **40**, 2940 (1989).

[6] T. Hashizume, E. Ikeda, Y. Akatsu, H. Ohno, and H. Hasegawa, Jpn. J. Appl. Phys. **23**, L296 (1984).

[7] S.S. Li, D.H. Lee, C.G. Choi, and J.E. Andrews, Appl. Phys. Lett. **47**, 1180 (1985).

[8] F.D. Auret, M. Nel, and A.W.R. Leitch, J. Cryst. Growth **89**, 308 (1988).

[9] A.S. Tabata, M.A.A. Pudensi, and A.M. Machado, J. Appl. Phys. **65**, 4076 (1989).

[10] A.W.R. Leitch, Th. Prescha, and J. Weber, Phys. Rev. B **44**, 1375 (1991).

[11] A.W.R. Leitch, Th. Prescha, and J. Weber, Phys. Rev. B **44**, 5912 (1991).

[12] S.J. Pearton and A.J. Tavendale, Electron. Lett. **18**, 715 (1982).

[13] W.C. Dautremont-Smith, J.C. Nabity, V. Swaminathan, M. Stavola, J. Chevallier, C.W. Tu, and S.J. Pearton, Appl. Phys. Lett. **49**, 1098 (1986).

[14] H.Y. Cho, E.K. Kim, S. Min, J.B. Kim, and J. Jang, Appl. Phys. Lett. **53**, 856 (1988).

[15] A. Jalil, A. Heurtel, Y. Marfaing, and J. Chevallier, J. Appl. Phys. **66**, 5854 (1989).

[16] M. Stutzmann and C.P. Herrero, in *Proceedings of the 20th International Conference on the Physics of Semiconductors, Thessaloniki, 1990*, edited by E.M. Anastassakis and J.D. Joannopoulos (World Scientific, Singapore, 1990), p. 783.

[17] G.M. Martin, A. Mitonneau, and A. Mircea, Electron. Lett. **13**, 191 (1977).

[18] J. Lagowski, M. Kaminska, J.M. Parsey, H.C. Gatos, and M. Lichtensteiger, Appl. Phys. Lett. **41**, 1078 (1982).

[19] U. Kaufmann, E. Klausmann, J. Schneider, and H.Ch. Alt, Phys. Rev. B **43**, 12 106 (1991).

[20] H.Y. Cho, E.K. Kim, S. Min, K.J. Chang, and C. Lee, Appl. Phys. Lett. **58**, 1866 (1991).

[21] H.Y. Cho, E.K. Kim, S.K. Min, and C. Lee, Phys. Rev. B **43**, 14 498 (1991).