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Ar plasma induced deep levels in epitaxial *n*-GaAs

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Ar plasma etching of *n*-type (Si doped) GaAs introduces several electron traps (E_c - 0.04 eV, E_c - 0.07 eV, E_c - 0.19 eV, E_c - 0.31 eV, E_c - 0.53 eV, and E_c - 0.61 eV). The trap, E_c - 0.04 eV, labelled E1′ and having a trap signature similar to irradiation induced defect E1, appears to be metastable. E_c - 0.31 eV and E_c - 0.61 eV are metastable too and they are similar to the M3/M4 defect configuration present in hydrogen plasma exposed *n*-GaAs. © *2012 American Institute of Physics*. [doi:10.1063/1.3673322]

I. INTRODUCTION

The introduction of defects by high energy alpha particles (α),[1] electrons (*β*),[2,3] protons (H^+),[4,5] neutrons,[6] and hydrogen plasmas[7,8] in GaAs has been studied extensively. To the best of our knowledge, no study on deep levels introduced by Ar inductively coupled plasma (ICP) etching of *n*-GaAs has been reported to date. This letter reports on the electronic properties of defects introduced by low energy ICP etching (using Ar) in epitaxial *n*-GaAs. A new defect with similar properties to the well documented E1 is detected. It is also shown that Ar plasma treatment introduces, apart from a number of other electron traps, a two defect metastable configuration. The signatures and transformation behaviour of these defects are similar to the M3/M4 metastable defects in GaAs grown by organo metalic vapour phase epitaxy (OMVPE) reported by Buchwald *et al.*[9] and subsequently by, amongst others, Leitch *et al.*,[8] Conibear *et al.*,[10] and Pfeiffer and Weber[11] following hydrogen plasma treatment of GaAs.

II. EXPERIMENTAL

Si doped (100) *n*-type epitaxial GaAs layers (5 μm) grown by OMVPE on n^+ GaAs substrates were used in this study. The average free carrier density (N_d) of the material, specified by the supplier (SPIRE Semiconductor) and confirmed by standard capacitance-voltage (*C*-*V*) measurements at 1 MHz, was 1.0×10^{15} cm^{-3}. Prior to device fabrication all samples were organically cleaned, etched, and de-oxidized following standard procedures.[3,4] Ohmic contacts were subsequently formed by depositing Ni-AuGe-Ni (5 nm/150 nm/45 nm) on the backside of the n^+ substrate, followed by annealing at 450 °C for 2 min in a 99.999% pure Ar atmosphere. The samples were again briefly etched and deoxidized before being exposed to low energy inductively coupled Ar plasma. The energy and dose rate of the Ar ions were 60 eV and 10^{15}/cm^{2}s, respectively. Pd Schottky barrier diodes (SBDs), 0.6 mm in diameter and 100 nm thick, were deposited onto the front surface of the samples as follows:

(1) *Sample A:* Resistive deposition (referred to as the reference).
(2) *Sample B:* Electron beam deposition (EBD).
(3) *Sample C:* Subjected to a 10 min ICP etch prior to EBD deposition.
(4) *Sample D:* 10 min ICP etch prior to EBD deposition, followed by megaelectron volt electron irradiation using a Sr^{90} source.

The SBD quality was assessed by *I*-*V* measurements using a programmable HP 4140B pA meter integrated with a DC voltage source. Deep level transient spectroscopy (DLTS) spectra were recorded at a scan rate of 3 K/min in the temperature range of 15–330 K using a rate window of 80 Hz. Unless stated otherwise the reverse bias and filling pulse was −2 V and 2 V, respectively. The pulse width, in all cases, was 1 ms. The electrical properties of the traps were analyzed using the well-known thermal emission rate (e_n) equation.[12–14] The activation enthalpy $E_c - E_T$ (the difference in energy between the bottom of the conduction band (E_c) and the defect level (E_T)), and apparent capture cross sections (σ_{na}) were determined from the slope and y-intercept, respectively, of a $\log(T^2/e_n)$ versus $(1000/T)$ Arrhenius plot. Laplace DLTS was used to resolve defects with narrowly spaced emission rates.

III. RESULTS

Fig. 1 shows DLTS spectra obtained from the reference, EBD and ICP etched and ICP etched + MeV *β*-irradiated samples labelled *A, B, C, and D*, respectively. No defects were observed in the as-grown material within the detection limit of the system used (10^{11} cm^{-3}). Extensive damage is however caused by EBD as evidenced by the single broad peak around 200 K. This defect is only detected upon employing a pulse exceeding 0.2 V suggesting that it probably originates from a continuum of defect states close to the surface of the epitaxial layer. Comparing *spectra B, C,* and *D*, it is evident that defects introduced by EBD are not

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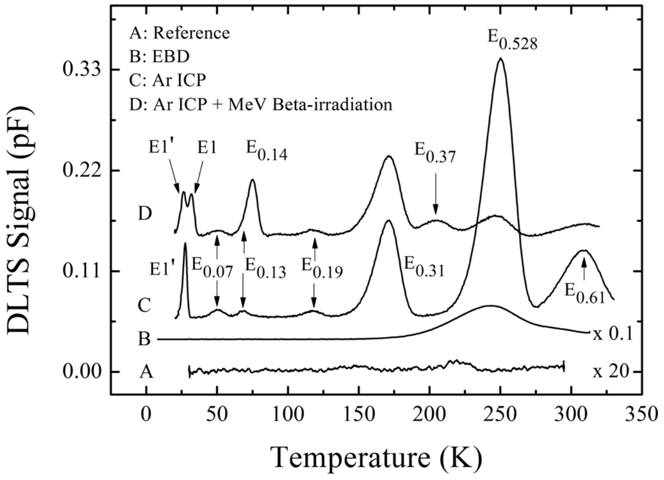

FIG. 1. DLTS spectra obtained from *samples A-D*. The spectra were recorded using a rate window of $80\,\mathrm{s}^{-1}$, a reverse bias of -2 V, and a filling pulse of 2 V. The pulse width in all cases was 1 ms.

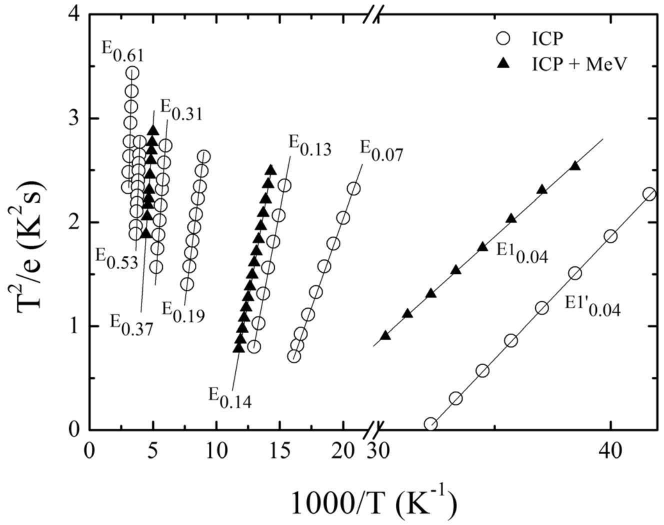

FIG. 2. Arrhenius plots for defects detected in OMVPE grown *n*-GaAs following Ar ICP etching (*sample C*) and ICP etching +MeV electron irradiation (*sample D*). The activation enthalpy for E1, E1′, and E_c - 0.61 were recorded at a reverse bias of -1 V.

detected in samples subjected to ICP etching (and ICP etching followed by MeV electron irradiation) prior to EBD. A similar observation was made by Auret *et al.*[15] upon investigating ICP etched Ge.

It is evident from Fig. 1 (*spectrum C*), that several electron traps, E_c - 0.04 eV (hereafter referred to as E1′), E_c - 0.19 eV, E_c - 0.31 eV, E_c - 0.53 eV, and E_c - 0.61 eV, are introduced by ICP etching. In addition to these, two minor peaks labelled E_c - 0.07 eV and E_c - 0.13 eV were also observed. For most of the defects a reverse bias of -2 V was used. The exceptions were E_c - 0.61 eV and E1′, for which considerable changes in the emission rate with reverse bias were observed. Consequently, the capture and emission dynamics of these traps were studied using a reduced reverse bias of -1 V and a filling pulse of 1 V, respectively. Fig. 1 (*spectrum D*) shows the defects introduced by Ar ICP etching followed by MeV electron irradiation. Clearly Ar plasma etching introduces a new set of defects not introduced by electron irradiation with the most significant being E1′, E_c - 0.31 eV, and E_c - 0.61 eV. It is instructive to note that E_c - 0.13 eV in spectrum C appears as a shoulder in the peak with activation energy, E_c - 0.14 eV present in *spectrum D* and identified as E2.

Fig. 2 depicts Arrhenius plots for the electron traps observed in the ICP etched (Fig. 1. *spectrum C*) and ICP etched followed by MeV electron irradiation (Fig. 1. *spectrum D*), samples, while Table I lists the activation energies (E_T) and temperature independent capture cross sections

TABLE I. Electronic properties of defects in ICP etched OMVPE grown *n*-GaAs. The peak temperatures were obtained at a rate window of $80\,\mathrm{s}^{-1}$.

ID	E_T (eV)	σ_{na} (cm^{-2})	Reference
E1′	E_c - 0.04	5.36×10^{-14}	This work
E1, EE1	E_c - 0.044 ± 0.001	$1.78 \times 10^{-15} \pm 0.56 \times 10^{-15}$	2, 3
Eα1, Eβ1, En1	E_c - 0.041	$5.86 \times 10^{-16} \pm 0.70 \times 10^{-16}$	16, 19
EAr1	E_c - 0.050	1×10^{-13}	17
E(0.07)	E_c - 0.07	1.03×10^{-15}	This work
E(0.13)	E_c - 0.13	3.56×10^{-13}	This work
E2, EE2, Eα2, Eβ2, En2	E_c - 141 ± 0.003	$1.0 \times 10^{-13} \pm 0.3 \times 10^{-13}$	2, 16, 18, 19
EAr3	E_c - 0.125	8×10^{-15}	17
E(0.19)	E_c - 0.19	5.99×10^{-13}	This work
EAr5	E_c - 0.19	8.0×10^{-14}	17
E(0.31) (M4?)	E_c - 0.31	5.26×10^{-14}	This work
E3, EE3, Eα3, PR4	E_c - 0.307 ± 0.003	$4.42 \times 10^{-15} \pm 2.60 \times 10^{-15}$	2, 16, 19, 20
M4 (H related)	E_c - 0.31	8×10^{-15}	9
M4 (H related)	E_c - 0.30		10
EAr8	E_c - 0.31	8×10^{-14}	12
E(0.53) (M4*?)	E_c - 0.53	5.88×10^{-13}	This work
M4*	E_c - 0.52		10
E(0.61) (M3?)	E_c - 0.61	7.71×10^{-14}	This work
M3 (H related)	E_c - 0.61		9
M3 (H related)	E_c - 0.55		10
Eα5, Ep5	E_c - 0.636 ± 0.001	$7 \times 10^{-13} \pm 0.2 \times 10^{-13}$	4, 11

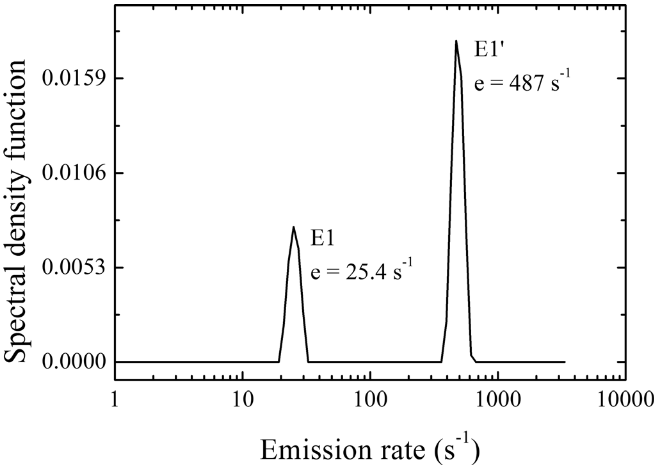

FIG. 3. Laplace DLTS spectrum recorded at 30 K obtained from *sample D*. The emission rate for E1 is higher by a factor 20 compared to that of E1′. The spectra were recorded using a reverse bias of −1 V and a filling pulse of 1 V. The pulse width was 1 ms.

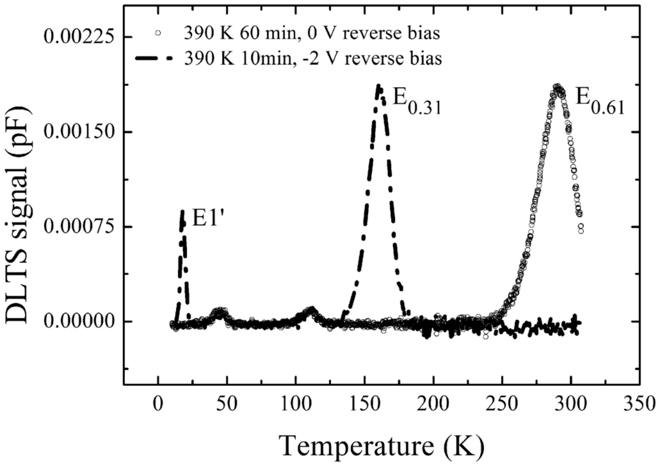

FIG. 4. DLTS spectra of the ICP etched material depicting the direct transformation between E_c - 0.31 eV and E_c - 0.61 eV. The metastable nature of E1′ is also clearly evident. The spectra were recorded using a rate window of 1.0 s^{-1}, a reverse bias of −2 V, and a filling pulse of 2 V. The pulse width was 1 ms.

(σ_{na}) pertaining to the observed traps. These trap signatures are compared to that of similar defects introduced by nuclear particle and electron irradiation in addition to Ar ion sputtering (2 keV) previously reported for *n*-GaAs. None of the defects previously reported for high energy particle and electron irradiated *n*-GaAs matches the E_c - 0.07 eV defect. This defect is consequently formed by the interaction of energetic species present in the Ar plasma with the exposed epitaxial layer. Trap signatures for E_c - 0.31 eV seem to compare favourably with signatures previously reported by various researchers for E3, Eα3, and EAr8 as listed in Table I. This defect is however metastable and has a capture cross section an order of magnitude lower than E3. It is clear from Table I that the activation enthalpy of E1′ compares well with that of the As vacancy related defect, E1, commonly observed in particle irradiated GaAs.[2,3,16,19] Notably, E1 and E1′ have similar signatures. It is therefore reasonable to assume that if the emission rates of these two defects cannot be resolved, incorrect identification can easily occur.

Fig. 3 shows the Laplace DLTS spectrum (i.e., the emission rate dependent spectral density function) for E1 and E1′ and confirms that they are indeed independent defects. Despite their similar activation energies, the emission rate of E1′ is larger by a factor of ~20 (at 30 K). The pulse width dependence of the capture dynamics show that a 100 ns pulse is sufficiently long to saturate E1′ whereas a pulse exceeding 10 μs is required to partially fill E1. From this observation it follows that E1 has a smaller capture cross section than that of E1′. These results provide convincing evidence that E1 and E1′ are different defects. Furthermore it is suggested that E1′ and EAr1, both being introduced by Ar related treatment, may possibly have the same origin.

From Fig. 4 it is evident that E_c - 0.31 eV transforms into E_c - 0.61 eV upon annealing under zero bias at 390 K for 60 min and can be completely recovered when annealing at 390 K for 10 min with a reverse bias of −2 V. E_c - 0.31 eV consequently appears to be similar to the metastable defect M4 (which transforms into M3 under similar conditions) observed in dc H-plasma treated GaAs and reported on by various authors.[8–10,21] It is also interesting to observe the direct correlation between the concentrations of E_c - 0.31 eV and E_c - 0.61 eV upon transforming from the one state to the other. This is contrary to observations made by both Buchwald *et al.*[9] and Conibear *et al.*[10] In addition, it is evident from Fig. 4 that E1′ is metastable too. The metastable counterpart could however not be detected in this study possibly because it is too deep for detection considering the experimental conditions employed. The transformation kinetics of this defect is currently being investigated.

The transformation of $E_{0.61} \rightarrow E_{0.31}$ (and $E_{0.31} \rightarrow E_{0.61}$) was found to obey first order kinetics with the isochronal temperature dependent defect concentration expressed by[9]

$$N(t,T) = N_0 \exp[1 - te_0(T)]. \tag{1}$$

The rate of transformation is given by

$$e_0 = \alpha \exp(-E/kT). \tag{2}$$

In the above two equations N_0 is the maximum defect concentration, t the anneal time (in seconds), and $e_0(T)$ the temperature dependent transformation rate, α, a pre-factor with units of s^{-1}, and E, the activation barrier for a particular transformation. The Arrhenius data for the trap transformation $E_{0.61} \rightarrow E_{0.31}$ and $E_{0.31} \rightarrow E_{0.61}$ is shown in Fig. 5. The $E_{0.61} \rightarrow E_{0.31}$ transformation is characterized by

$$e_0 = 2.84 \times 10^{19} \exp(-1.72/\mathrm{kT}), \tag{3}$$

and the reverse transformation by

$$e_0 = 5.04 \times 10^{14} \exp(-1.38/\mathrm{kT}). \tag{4}$$

The $E_{0.61} \rightarrow E_{0.31}$ transformation barrier (E) agrees well with that for M3 → M4 reported by Buchwald *et al.*[9] but is higher by a factor of ~2 and ~1.5, respectively, compared to values reported by Conibear *et al.*[10] and Pfeiffer and Weber.[11] The pre-factor (in all these reports) shows very little agreement

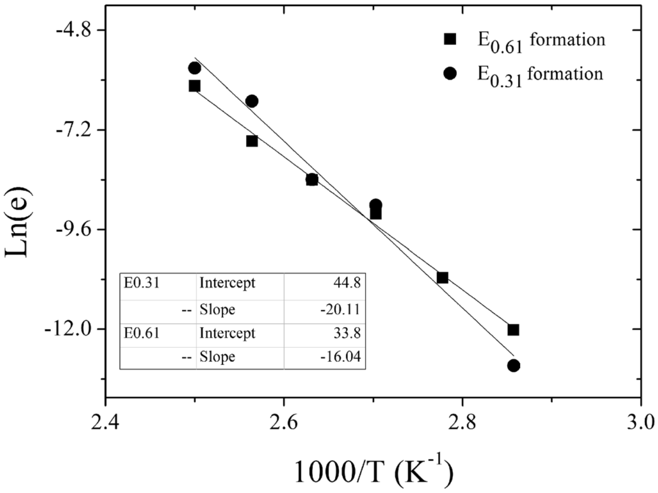

FIG. 5. Arrhenius data for the $E_{0.61} \rightarrow E_{0.31}$ and $E_{0.31} \rightarrow E_{0.61}$ (M3 → M4? and M4 → M3?) trap transformations.

and ranges from 10^8–$10^{21}\,s^{-1}$. Similar observations were made for the M4 ⟶ M3 transformation.

IV. CONCLUSIONS

Conventional DLTS and high resolution Laplace DLTS were used to study defects introduced by ICP Ar etching of *n*-type (Si doped) GaAs. Results reveal that ICP etching introduces several electron traps of which two, E_c - 0.07 eV and a metastable defect, E1′, with activation enthalpy similar to E1 have been observed. The subsequent irradiation of the ICP etched material with MeV electrons allowed the simultaneous observation of both E1′ and E1. The emission rate of E1′ at 30 K was found to be larger than that measured for E1 by a factor of ∼20. Finally, E_c - 0.31 eV is a metastable defect which transforms into E_c - 0.61 eV upon annealing at 390 K for 60 min under zero bias. This defect appears to be similar to the M4/M3 metastable defect states observed in dc H-plasma treated GaAs. The results presented here suggest that the M4/M3 metastable configuration may not be related to hydrogen[9,10] and/or oxygen[11] as previously thought.

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