Inductively coupled plasma induced deep levels in epitaxial *n*-GaAs

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The electronic properties of defects introduced by low energy inductively coupled Ar plasma etching of *n*-type (Si doped) GaAs were investigated by deeplevel transient spectroscopy (DLTS) and Laplace DLTS. Several prominent electron traps (E_c—0.046 eV, E_c—0.186 eV, E_c—0.314 eV. E_c—0.528 eV and E_c—0.605 eV) were detected. The metastable defect E_c—0.046 eV having a trap signature similar to E1 is observed for the first time. E_c—0.314 eV and E_c—0.605 eV are metastable and appear to be similar to the M3 and M4 defects present in dc H-plasma exposed GaAs.

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1. Introduction

Inductively coupled plasma (ICP) etching is routinely used in semiconductor device technology to remove impurities and contaminants from surfaces of materials prior to device fabrication. The process involves the bombardment of the relevant surface with various energetic species including atoms, molecules, ions, electrons and photons, all being constituents of the gas plasma. While the intention is to clean the surface from such contaminants and simultaneously improve its morphology these particles are known to introduce electrically active defects close to the metal–semiconductor junction, consequently affecting the barrier height and device performance.

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. In order to identify the observed defects, their signatures are compared to those of defects ensuing from *α, β,* H^+ and neutron irradiation, as well as Ar ion sputtering in *n*-GaAs reported in literature.

2. 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 x 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 a 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:

i) *Sample A:* Resistive deposition (referred to as the reference).

ii) *Sample B:* Electron beam deposition (EBD).

iii) *Sample C:* Subjected to a 10 minute ICP etch prior to EBD deposition.

iv) *Sample D:* 10 minute ICP etch prior to EBD deposition, followed by MeV electron irradiation using a Sr^{90} source.

Schottky contact deposition was performed in a vacuum better than 10^{-5} mbar regardless of the processes and system used. Ten minute Ar plasma etches were performed using a Copra DN200 inductivelycoupledplasma beam source. The energy and dose rate of the plasma ions were 60 eV and 10^{15}/cm^{-2}s, respectively.

The SBD quality was assessed by the **I–V** measurements using a programmable HP 4140B pA metre integrated with a DC voltage source. 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. The reverse bias was –2 V, while the filling pulse amplitude was 2 V. The width of the filling pulse was 1 ms unless stated otherwise. The electrical properties of the traps were analysed using the thermal emission rate equation [9]

$$e_n = \sigma_{na} \gamma_n T^2 e^{-(E_c - E_T)/kT} \tag{1}$$

Here, $\mathbf{e}_n$ is the electron emission rate at a given temperature **T, k** is the Boltzmann constant and $\boldsymbol{\gamma}_n$ equal to $(N_c \langle \mathbf{v}_n \rangle / \mathbf{T}^2) g_0/g_1$ and has the value 2.21×10^{20} cm^{-2}s^{-2}K^{-2} for an electron trap [10] and [11]. N_c is the density of states in the conduction band, $\langle \mathbf{v}_n \rangle$ the average thermal velocity of the electrons and g_0 and g_1 are degeneracy terms related to the defect state before and after electron emission. The activation energy $\mathbf{E}_c - \mathbf{E}_T$ (the difference in energy between the bottom of the conduction band ($\mathbf{E}_c$) and the defect level ($\mathbf{E}_T$)) and apparent capture cross sections, $\boldsymbol{\sigma}_{na}$, were determined from the slope and y-intercept, respectively, of a log($\mathbf{T}^2/\mathbf{e}_n$) versus (1000/**T**) Arrhenius plot. The Laplace DLTS was used to resolve the structure of the low-temperature peak at about 30 K.

3. Results

Fig. 1 (a) shows DLTS spectra obtained from the reference, EBD and ICP etched samples labelled A, B and C, respectively. No defects with concentrations exceeding $10^{12}\,\mathrm{cm}^{-3}$ were observed in the as-grown material. However, extensive damage is caused by the EBD treatment as evidenced by the single broad peak around 200 K. This peak is only detected upon employing a filling pulse exceeding 0.2 V, suggesting that it could originate from a continuum of defect states close to the *n*-GaAs epilayer surface. Comparing spectra B and C, it is evident that defects introduced by EBD are not detected in samples subjected to ICP etching prior to the EBD. Auret et al. [12] reported a similar observation when comparing electron beam deposited Pd SBDs on Ge to samples exposed to ICP etching prior to EBD of the SBDs.

It is evident from Fig. 1 (spectrum C) that several electron traps $\mathbf{E}_c$—0.046 eV, (hereafter referred to as E1′) $\mathbf{E}_c$—0.186 eV, $\mathbf{E}_c$—0.314 eV, $\mathbf{E}_c$—0.528 eV and $\mathbf{E}_c$—0.605 eV were introduced by ICP etching. In addition to these, two other minor peaks labelled $\mathbf{E}_c$—0.070 eV and $\mathbf{E}_c$—0.128 eV were also observed in the DLTS spectrum. One should mention that the DLTS spectra were recorded with a reverse bias and filling pulse of –2 V and 2 V, respectively. For most of the defects the electrical field induced by the bias was sufficiently low to avoid field-enhanced emission (causing erroneous activation energy values). The exceptions were $\mathbf{E}_c$—0.605 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

Fig. 2 depicts Arrhenius plots for the electron traps observed in the ICP etched sample in Fig. 1. The signatures were derived from data acquired using a reverse bias of –2 V and a filling pulse of 2 V, except for the $\mathbf{E}_c$—0.046 (E1′) and $\mathbf{E}_c$—0.605 eV for reasons already explained. Table 1 lists the activation energies ($\mathbf{E}_T$) and temperature independent capture cross sections ($\boldsymbol{\sigma}_{na}$) pertaining to all the defects introduced by Ar ICP etching. These signatures are compared to those of similar defects introduced by nuclear particle and electron irradiation in addition to Ar ion sputtering (2 keV) previously reported for *n*-GaAs. It is clear from Table 1 that the activation energy of E1′ matches that of the As vacancy related defect, E1, commonly observed in particle irradiated GaAs. However, $\boldsymbol{\sigma}_{na}$ for E1′ obtained in this study is about 300–500 times larger, consequently casting doubt over whether the two are indeed related. Similarly, signature obtained for E1′ does not correlate well with that of Eα1, Eβ1 and En1 previously reported in different studies. The capture rate as function of pulse width showed that E1 was not observed when employing a pulse width of 200 ns whereas the E1′ peak height was only reduced by 25% as compared to the height at 1 ms. Further evidence that E1 and E1′ are very likely to originate from different defects is provided below.

None of the defects previously reported for high energy particle and electron irradiated *n*-GaAs matches the $\mathbf{E}_c$—0.070 eV defect. It is concluded that this defect is formed by the interaction of energetic species present in the Ar plasma with the exposed epitaxial layer. (It is instructive to note that the ICP plasma does not exclusively contain Ar ions and that other species may also introduce electrically active defects.) Trap signatures for $\mathbf{E}_c$—0.314 eV seem to compare favourably with signatures previously reported by various researchers for E3, Eα3 and EAr8 as listed in Table 1. This defect unlike the latter is metastable and has a capture cross section an order of magnitude lower than compared to E3. It is instructive to note that $\mathbf{E}_c$—0.314 eV transforms into $\mathbf{E}_c$—0.605 eV upon annealing under zero bias at 390 K for 60 min (not shown here). The transformation is completely reversible upon annealing at 390 K for 10 min with a reverse bias of –2 V. $\mathbf{E}_c$—0.314 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], [18], [19] and [20]. In addition, E1′ has been found to be metastable too. The metastable counterpart of this defect could however not be detected, possibly because it is too deep for detection considering the experimental conditions employed. The transformation kinetics of these defects are currently being investigated.

Fig. 3 depicts a DLTS spectrum (10 K–50 K) obtained from the epitaxial*n*-GaAs layer exposed to ICP etching in addition to electrons (MeV) from a ^{90}Sr source (sample C′). Electron irradiation introduces three peaks, the well documented E1, E2 and E3 (E2 and E3 not shown here). Notably, E1 and E1′ have similar trap signatures. It is therefore reasonable to assume that one of the defects can be mistaken for the other and can consequently easily be identified incorrectly. From Table 1, E1′ probably best matches the signature of the Ar sputter induced trap, labelled EAr1, often compared in literature with E1 and suggested to have the same origin. The result presented here provides convincing evidence that E1 and E1′ are two different defects and secondly that the E1′ and EAr1, both being introduced by Ar related treatment, most probably have the same origin. Further investigation is however required to confirm this.

Additional evidence that E1 and E1′ are indeed uniquely different was obtained from the emission rate dependant spectral density function using the Laplace DLTS technique. Despite their similar activation energies, the emission rate of E1′ was found to be larger by a factor of ~25 (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′.

4. Conclusions

Conventional 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—0.070 eV and a metastable defect labelled E1′ with activation energy similar to E1 have been observed for the first time. Irradiating the ICP etched material with MeV electrons too, 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 ~25. It is clear than none of the defects introduced by ICP etching are introduced by MeV electron irradiation. This implies that the ICP etch process introduces defects of a more complex nature.

Finally, E_c—0.314 eV is a metastable defect, which transforms into E_c—0.605 eV upon annealing at 390 K for 60 min under zero bias. This defect appears to be the similar to the M4/M3 metastable defect observed in dc H-plasma treated GaAs.

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Table I.

Electronic properties of defects in ICP etched OMVPE grown *n*-GaAs. The peak temperatures were obtained at a rate window of 80 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}	17
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

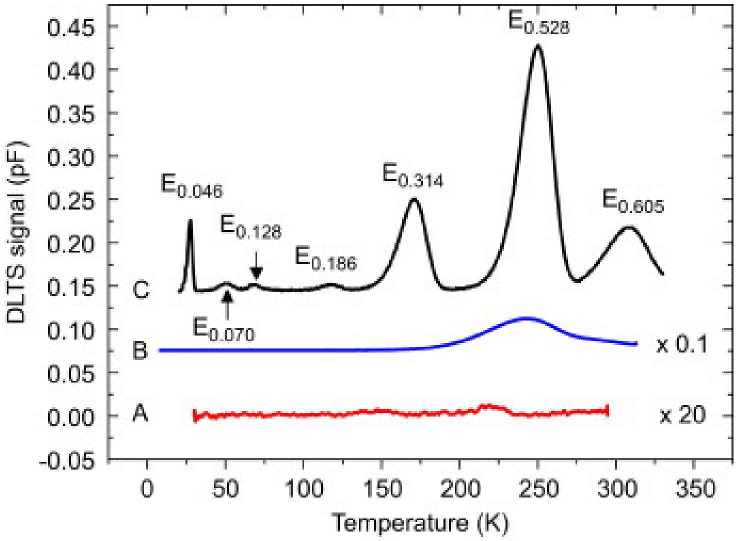

Fig.1. DLTS spectra obtained from *samples A-D*. The spectra were recorded using a rate window of 80 s^{-1}, a reverse bias of -2 V and a filling pulse of 2 V. The pulse width in all cases was 1 ms.

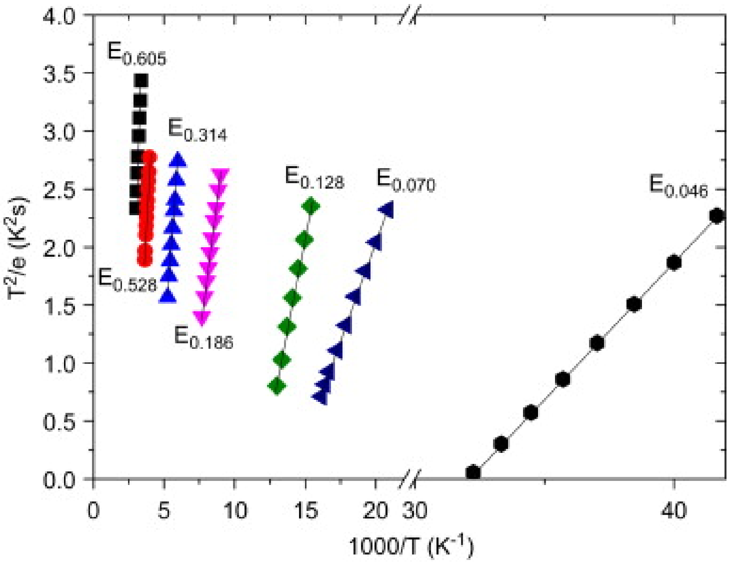

Fig. 2. Arrhenius plots for defects introduced by ICP etching of the OMVPE grown *n*-GaAs.

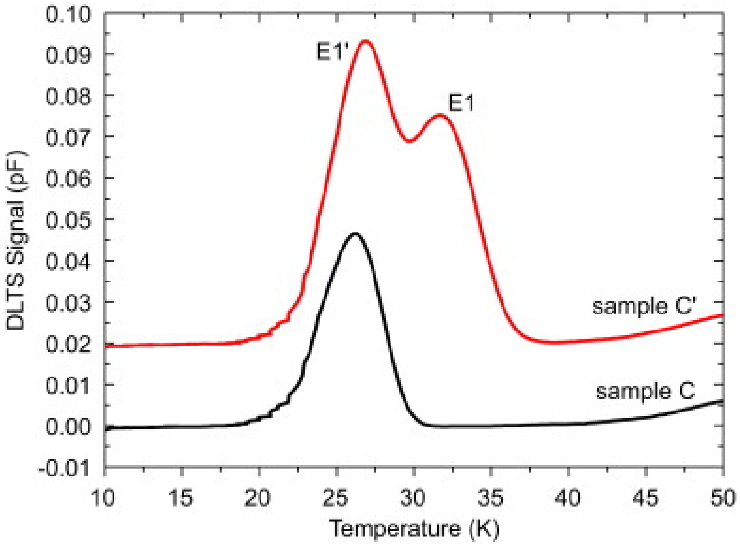

Fig. 3. DLTS spectra for sample C, the ICP etched, and C′, the ICP etched+MeV electron irradiated sample. The spectra were recorded using a rate window of 80 s^{-1}, a reverse bias of –1 V and a filling pulse of 1.4 V.