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## PASSIVATION OF A BULK DEFECT $E_C-0.22$ eV IN GaAs BY CONTACT WITH PHOSPHORIC ACID\*

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The  $E_C-0.22$  eV trap in Horizontal Bridgman undoped  $n$ -type GaAs may be passivated by contact with phosphoric acid for 8 hours at room temperature. Isochronal annealing, at around  $250^\circ\text{C}$  for 1 hour resulted in the partial recovery of this defect. The possible mechanisms of  $E_C-0.22$  eV trap passivation are proposed.

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The electronic properties of GaAs depend critically on the localized levels in the forbidden gap. The technological procedures during semiconductor device processing often involve the contact of chemicals like acids or solvents with the semiconductor surface. It has been noticed only recently that these treatments are not as benign as they had been thought and they are capable to change the semiconductor properties [1]. It is our aim to report on the changes of defect concentration in bulk GaAs detected by DLTS (Deep Level Transient Spectroscopy) when GaAs is in contact with phosphoric acid in ambient temperature. We propose that these changes are due to hydrogen diffusion into the near-surface region of the samples. The source of hydrogen is the acid itself.

The material examined was undoped ( $n = 1.5 \times 10^{15} \text{ cm}^{-3}$ ) Horizontal Bridgman GaAs grown in MIT (USA). Two sets of samples were prepared. The samples from the first set were measured and then immersed in 60%  $\text{H}_3\text{PO}_4$  at room temperature for 8 h. Afterwards they were annealed isochronally for 1 h between  $200^\circ\text{C}$  and  $300^\circ\text{C}$  in vacuum ( $5 \times 10^{-5}$  Torr). The samples were heated from room temperature to final annealing temperature in 5 min. The samples from the second set were subjected to electrolysis in 60%  $\text{H}_3\text{PO}_4$  at room temperature for 8 h. They served as a cathode of electrochemical cell with Pt foil as an anode. The current density was  $1 \text{ A/cm}^2$ . The DLTS spectrum of as-grown material revealed 4 peaks

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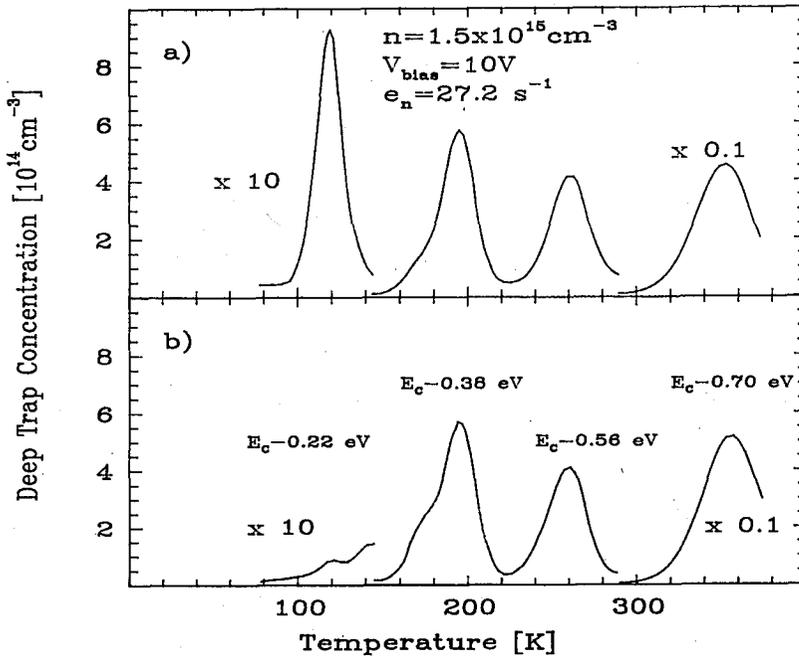


Fig. 1. DLTS spectra for as-grown GaAs (a) and for GaAs after electrolysis in  $\text{H}_3\text{PO}_4$  (b).  $V_{\text{bias}}$  is the reverse bias voltage and  $e_n$  is the emission window rate. Parameters of observed traps:  $E_c - 0.22 \text{ eV}$ ,  $\sigma_\infty = 1.4 \times 10^{-14} \text{ cm}^2$ ;  $E_c - 0.38 \text{ eV}$ ,  $\sigma_\infty = 5.4 \times 10^{-14} \text{ cm}^2$ ;  $E_c - 0.56 \text{ eV}$ ,  $\sigma_\infty = 4.8 \times 10^{-13} \text{ cm}^2$ ;  $E_c - 0.70 \text{ eV}$ ,  $\sigma_\infty = 1.5 \times 10^{-14} \text{ cm}^2$ .

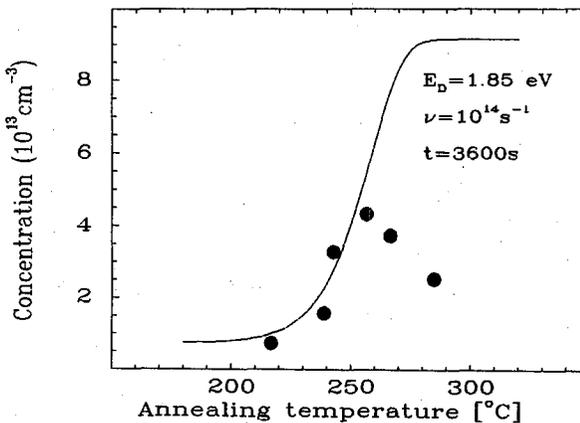
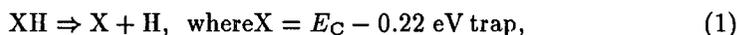


Fig. 2.  $E_c - 0.22 \text{ eV}$  trap concentration in  $\text{H}_3\text{PO}_4$  soaked (8 h) and isochronal annealed (1h) samples. Smooth line is the expected concentration calculated from the first order kinetics.

(see Fig. 1a). The energies and majority-carrier cross-sections of corresponding levels were obtained from Arrhenius plots ( $e_n/T^2$  vs.  $1/T$ , where  $e_n$  is the emission rate and  $T$  is the temperature). Observed levels are common in this type of GaAs crystals [2-4]. The samples which were in contact with  $H_3PO_4$  revealed the ten-fold decrease of the  $E_C-0.22$  eV trap concentration (from  $9.1 \times 10^{13} \text{ cm}^{-3}$  in as-grown material to  $7.2 \times 10^{12} \text{ cm}^{-3}$  in acid-soaked samples and to  $5.7 \times 10^{12} \text{ cm}^{-3}$  in samples subjected to electrolysis) (see Fig. 1b). Within experimental accuracy the concentration of remaining traps as well as the free electron concentration after immersion in  $H_3PO_4$  remained the same. After isochronal annealing of acid-soaked samples the  $E_C-0.22$  eV trap concentration increased (see Fig. 2). The increase was greatest for the annealing at  $260^\circ \text{C}$ , but the concentration did not attain the  $E_C-0.22$  eV trap concentration in as-grown material. We propose, that the reduction of  $E_C-0.22$  eV trap concentration is due to its passivation by H. Hydrogen is abundant in highly dissociated phosphoric acid, therefore during immersion hydrogen diffusion and its binding to  $E_C-0.22$  eV trap can take place. It can be expected that H is only weakly bound to  $E_C-0.22$  eV trap. The relatively mild heating should destroy H binding and release  $E_C-0.22$  eV trap levels. Indeed, after heating to  $260^\circ \text{C}$  the  $E_C-0.22$  eV level reappears, at least partially. If we assume the first order kinetics of H dissociation [5], that means the dissociation reaction of the form:



we get

$$N_X = N_0 - N_{XH} \times \exp(-t \times \nu \times \exp(-E_D/kT)), \quad (2)$$

where  $N_X$  is the concentration of  $E_C-0.22$  eV trap in acid-soaked samples after annealing for time  $t$  at temperature  $T$ ,  $N_0$  is the  $E_C-0.22$  eV trap concentration in as-grown material,  $N_{XH}$  is the concentration of passivated  $E_C-0.22$  eV centers before annealing,  $k$  is the Boltzmann constant,  $\nu$  is the attempt frequency and  $E_D$  is the dissociation energy. If we take the attempt frequency equal to  $10^{14} \text{ s}^{-1}$  (comparable to the characteristic phonon frequency), we can deduce the H dissociation energy. The best fit gives  $E_D = 1.85 \pm 0.03$  eV (see Fig. 2). Such low dissociation energy is close to the dissociation energy of other H-donor complexes [6], of the order of 2 eV. For higher temperature the experimental points deviate substantially from the theoretical curve described by (2). It is possible that another phenomenon apart from XH complex decomposition becomes important. We guess that after further heating the X center itself decomposes and thus the concentration of  $E_C-0.22$  eV level decreases.

The concentration of  $E_C-0.22$  eV trap in bulk GaAs after immersion in  $H_3PO_4$  decreases. This reduction is probably due to direct H binding to the defect responsible for  $E_C-0.22$  eV level. This binding is weak ( $E_D=1.85$  eV) and can be destroyed by heating to  $270^\circ \text{C}$  for 1h. The heating at  $350^\circ \text{C}$  for 1h destroys  $E_C-0.22$  eV trap itself.

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