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NEUTRALISATION OF POINT DEFECTS IN Ge AND GaAs BY HYDROGEN INCORPORATION

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ABSTRACT

Deep level transient spectroscopy has been used to observe the passivation of copper-related centres in Ge, γ-radiation induced centres in Ge and residual defects in GaAs by reaction with atomic hydrogen. Data are presented on the efficiency of passivation as a function of the duration and temperature of the exposure to hydrogen. A 3-hour exposure in an H plasma at 300°C passivated >90% of the copper centres in Ge to a depth of $\sim$80 μm; 3 hours at 250°C passivated 3×10^{15} donor defects cm^{-3} to a depth of $\sim$1.1 μm in GaAs. An estimate of 3.5×10^{-9} cm^2 s^{-1} at 300°C was obtained for the diffusion coefficient of H in Ge; at 225°C the corresponding number for GaAs is estimated to be $\sim 3 \times 10^{-13}$ cm^2 s^{-1}.

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HYDROGEN; GALLIUM ARSENIDES; GERMANIUM; PASSIVATION; POINT DEFECTS; SEMICONDUCTOR MATERIALS; COPPER; GAMMA RADIATION; VACANCIES

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1. INTRODUCTION

There is considerable interest in the properties of hydrogen incorporated into amorphous and crystalline semiconductors, particularly silicon [Pankove et al. 1978, Pankove and Carlson 1980, Seager and Ginley 1979]. The passivation of dangling bonds by reaction with the H atom leads to lower leakage currents in p-n junctions [Pankove et al. 1978], improved efficiency of silicon solar cells [Pankove and Carlson 1980] and reduction of grain boundary recombination rates in polycrystalline Si [Seager and Ginley 1979]. Recently, direct observation of the hydrogen passivation of recombination centres caused by laser irradiation (located $\sim 1\ \mu m$ into the bulk of the material) has been reported for bulk silicon [Benton et al. 1980] using deep level transient spectroscopy (DLTS) [Lang 1974]. This has raised the possibility of passivating defects during device processing and fabrication but, as yet, little data has been published on the efficiency and depth of hydrogen passivation in Ge and GaAs as a function of the duration and temperature of the exposure to atomic hydrogen. Lithium passivation of γ-ray induced acceptor centres in Ge has been observed at this laboratory [Pearton & Tavendale - report in preparation] but, since Li is electrically active in Ge and Si, the use of inactive hydrogen would have obvious advantages.

Results are reported of experiments on Ge designed to measure the suitability of hydrogen neutralisation of bulk point defects related to γ-ray damage, copper contamination during processing, and defects incorporated during the crystal growth of GaAs.

2. EXPERIMENTAL

The Ge used in this work contained point defects of one of two types - γ-induced defects or contaminating copper centres. Gamma-induced defects were introduced into locally grown P- and As-doped n-type material ($N_D - N_A = 4 \times 10^{12} - 2 \times 10^{14}\ cm^{-3}$), Hoboken (Belgium) n-type material ($N_D - N_A = 5 \times 10^{13}\ cm^{-3}$) and high purity p-type Ge ($N_A - N_D = 3 \times 10^{10} - 7 \times 10^{11}\ cm^{-3}$) obtained from two US laboratories,General Electric (GE) and Lawrence Berkeley Laboratory (LBL). P-type samples were prepared in the usual fashion with Li diffused (5 min at 250°C) contacts on one face, and evaporated Pd ohmic contacts on the opposite face. N-type samples had GaIn 'rub-on' ohmic contacts with Pd surface barrier front contacts. Irradiations were performed in a $1.6 \times 10^4\ Gy\ h^{-1}$ ^{60}Co facility; n-type material received a dose of 1.5×10^6 Gy, and the p-type material 5×10^5 Gy. A second set of p-type samples from the same sources was also used - these had Sb-diffused (one hour at 500°C) n^+ contacts. During diffusion, significant concentrations of copper-related centres were introduced.

The net doping densities of the samples were in the range 2×10^{11} - 4×10^{13} cm^{-3} at 77 K, before irradiation.

The GaAs was n-type, polycrystalline bulk material ($N_D - N_A = 2 \times 10^{16}$ cm^{-3}) obtained from Mining and Chemical Products (MCP) Electronics (UK). Ohmic contacts were fabricated [Eberhardt et al. 1971] by alloying GaIn eutectic to the rear face of each sample, and a front rectifying contact (2 mm diameter) was obtained by Au evaporation. Two deep donor states have previously been measured in this material [Pearton et al. 1980].

Samples were tested on a DLTS system in four stages: (i) as processed; (ii) after heating for a specified time at a specified temperature in molecular hydrogen; (iii) after heating in atomic hydrogen for the same conditions as in (ii); and (iv) after heating in vacuum to evolve some of the atomic hydrogen. Separate samples were used for each set of plasma exposure conditions to avoid the possibility of too many heating cycles thickening the diffused contacts.

Samples were exposed to atomic hydrogen by insertion in a 0.5 W cm^{-3} (limiting upper value), 27 MHz hydrogen plasma, at a pressure of approximately 65 Pa* . The plasma was created by inductively coupling RF power via a coil enveloping a quartz tube; the samples were mounted on a high purity Ge substrate placed on a heater block. The hydrogen gas was purified by passing it through a Pd diffuser at 200°C, and then entered the top of the quartz tube in which the samples were mounted. A vacuum system incorporating a turbo molecular pump maintained the required pressure [Alexiev - report in preparation]. All of the heat treatments were performed in the same system.

3. RESULTS

3.1 Copper-related Centres in Ge

A typical DLTS spectrum for an as-processed Sb contacted p-type Ge sample is shown in Figure 1(a). The two peaks are due to a Cu-H complex [Haller et al. 1977] (E_V + 0.19 eV) and the doubly ionised Cu level [Woodbury and Tyler 1957; Milnes 1968; Haller et al. 1977] (E_V + 0.33 eV). The concentration of the Cu^{2-} level was in the range 2×10^{10} - 1×10^{13} cm^{-3}, constant to depths >200 μm. Heating in molecular hydrogen had no significant effect on the concentration or profile of these levels (Figure 1(a)).

Heating in a hydrogen plasma was carried out for periods between 0.5 and three hours at temperatures of 150-300°C, and significant neutralisation of the copper related centres was observed. Figure 1(c) shows the DLTS spectrum of the sample from Figures 1(a) and (b) after heating in the plasma for three hours at 300°C. The sample capacitance was also reduced, confirming the evidence of

* 1 Pa ≈ 7.5×10^{-3} torr

the DLTS trace that deep defect states had been neutralised. Figure 2 shows a series of capacitance-voltage curves for a sample exposed to the hydrogen plasma. The net doping density is reduced not only at 180 K but also at 77 K. At 180 K most of the Cu-H and Cu^{2-} levels will be ionised; the reduction in capacitance at this temperature is due to the neutralisation of these levels by the hydrogen. At 77 K, most of the Cu-H and Cu^{2-} will be frozen out; in this case the reduction in capacitance will be due to neutralisation of copper-related defects below 77 K, most notably the singly ionised copper level at E_V + 44 meV. [Woodbury and Tyler 1957; Milnes 1968; Haller et al. 1977]. The fact that hydrogen is acting to neutralise the copper centres is evident after hydrogenated samples have been annealed in vacuum - evolution of the hydrogen brings an increase in the density of electrically active defects (Figure 1(d)) and hence the capacitance of the sample (Figure 2).

Figure 3 shows the normalised concentration profile of the Cu^{2-} level (obtained from DLTS measurements) as a function of the plasma exposure conditions. In this pure Ge only small bias pulses are needed to cover relatively large distances (tens of μm) and, because of the unusual profile encountered in this experiment (a low but not negligible concentration for a distance followed by a rapid increase over a short distance) and the method of obtaining the profile (comparison of output signals for small changes in bias pulse amplitude), large errors can be present when determining certain points. Only those points are shown on which reliance can be placed. The concentrations are accurate to ±30%, and the distances to ±20%.

Extrapolation to the original concentration of the 3 hours, 300°C exposure graph given in Figure 3 would give an approximate lower limit H diffusion coefficient of $D_H = 3.5 \times 10^{-9}$ cm^2 s^{-1} at 300°C, i.e. diffusion depth = $(2 D_H \cdot \text{diffusion time})^{\frac{1}{2}}$. At 430°C, Hall and Soltys [1978] have obtained a diffusion coefficient of $\sim 2 \times 10^{-8}$ cm^2 s^{-1}. Extrapolating the results of Frank and Thomas [1960] who measured the diffusion coefficient at 800-910°C and found a coefficient of

$$D_H \doteq 2.7 \times 10^{-3} \exp\left(-\frac{0.38}{kT}\right) \text{ cm}^2 \text{ s}^{-1}$$

would give

$$D_H(300°\text{C}) = 1.2 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1} \quad .$$

It is likely that high temperature measurements cannot be extrapolated to lower temperatures because much of the hydrogen is in molecular form at lower temperatures [Hall and Soltys 1978].

Similar hydrogen passivation results were obtained with donor levels in an n-type sample deliberately diffused with Pd or Ag. It is likely that passivation

of many metal-related centres can be achieved - Cu is obviously the most important. The passivation mechanism in the case of Cu might be the conversion of all centres to $Cu\text{-}H_3$, which is assumed to be neutral [Haller et al. 1977].

3.2 Gamma-induced Centres in Ge

DLTS spectra from an n-type Hoboken sample containing a thermally stable deep donor level (E_c - 0.36 eV), and exposed to the H plasma for three hours at 150°C are shown in Figure 4. Reduction in electrical activity of the donor centre was evident to depths of approximately 30 μm. The sample was then heated in the plasma for four hours at 350°C, neutralising the donor levels to depths >80 μm. However an anneal in vacuum at the same temperature did not affect the sample. Possibly the hydrogen bonding to the donor defect is quite stable at these temperatures. A similar effect was seen with the E_c - 0.42 eV donor level in the As-doped sample (Figure 5). Hydrogenation for four hours at 350°C produced neutralisation of some of the donor levels, but annealing in vacuum under the same conditions after hydrogenation did not affect the material.

Samples of Ge and LBL material prepared with Li contacts, and then irradiated,also showed some neutralisation of the E_V + 0.23 eV and E_V + 0.38 eV acceptors after hydrogenation for two to three hours at 200°C, that was over and above the reduction due to thermal annealing of the centres. [Pearton & Tavendale - report in preparation]. These levels are also passivated by Li ions [Pearton & Tavendale - report in preparation]. The fact that Li contacts were used on these samples, and that the γ-induced centres start annealing at ∿200°C, precluded any further measurements on these levels.

3.3 Bulk Donors in GaAs

Considerable passivation by reaction with atomic hydrogen of the E_c - 0.36 eV donor level in this material was observed. Figure 6 shows the DLTS spectra for a sample hydrogenated for three hours at 250°C, and then annealed in vacuum. Under these conditions, $\sim 3 \times 10^{15}$ donors cm^{-3} are neutralised to a depth of 1.1 μm, as shown in Figure 7. Extrapolation of the three hours, 225°C exposure graph to the original concentration would give an approximate H diffusion coefficient of 3×10^{-13} cm^2 s^{-1} at 225°C. At 100°C the corresponding number is $\sim 2.2 \times 10^{-13}$ cm^2 s^{-1}. Concentration profiles of passivated levels as a function of plasma exposure conditions, such as those in Figures 3 and 7, could be used as possible methods of measuring the low temperature diffusion coefficients and solubility of hydrogen in semiconductor materials which are in general not well known.

It should be noted that the E_c - 0.70 eV level was not passivated by the hydrogen plasma treatment.

4. DISCUSSION AND SUMMARY

Significant reduction of the electrical activity of point defects in Ge by reaction with atomic hydrogen has been observed. The point defects were caused by copper contamination (or, in some cases, Ag or Pd) and by γ-irradiation. The depth of passivation under the plasma conditions used here is typically 100 μm for three hours at 300°C. Neutralisation of a donor state in GaAs has also been observed, but an important point arose during these investigations - another deep donor was not passivated by the same treatment. Also, the hydrogen diffusion coefficient in GaAs appears to be considerably lower than the corresponding value in Ge at the same temperature, and passivation of defects to depths of $\sim$ 1 μm for three hour exposures at 250°C in a hydrogen plasma is observed.

It is likely that the microscopic structure of point defects will determine their susceptibility to neutralisation by hydrogen incorporation. In such a case, some defects may require higher temperature plasma treatment, and others may not be passivated at any temperature. As was the case after the initial flush of enthusiasm for laser annealing of semiconductors, it is more than likely that hydrogen passivation will be a useful tool only in certain areas, but not a universal panacea for the problem of deep level impurities in semiconductors in general. Further experiments should more clearly delineate the useful areas of hydrogenation of bulk semiconductors.

5. ACKNOWLEDGEMENTS

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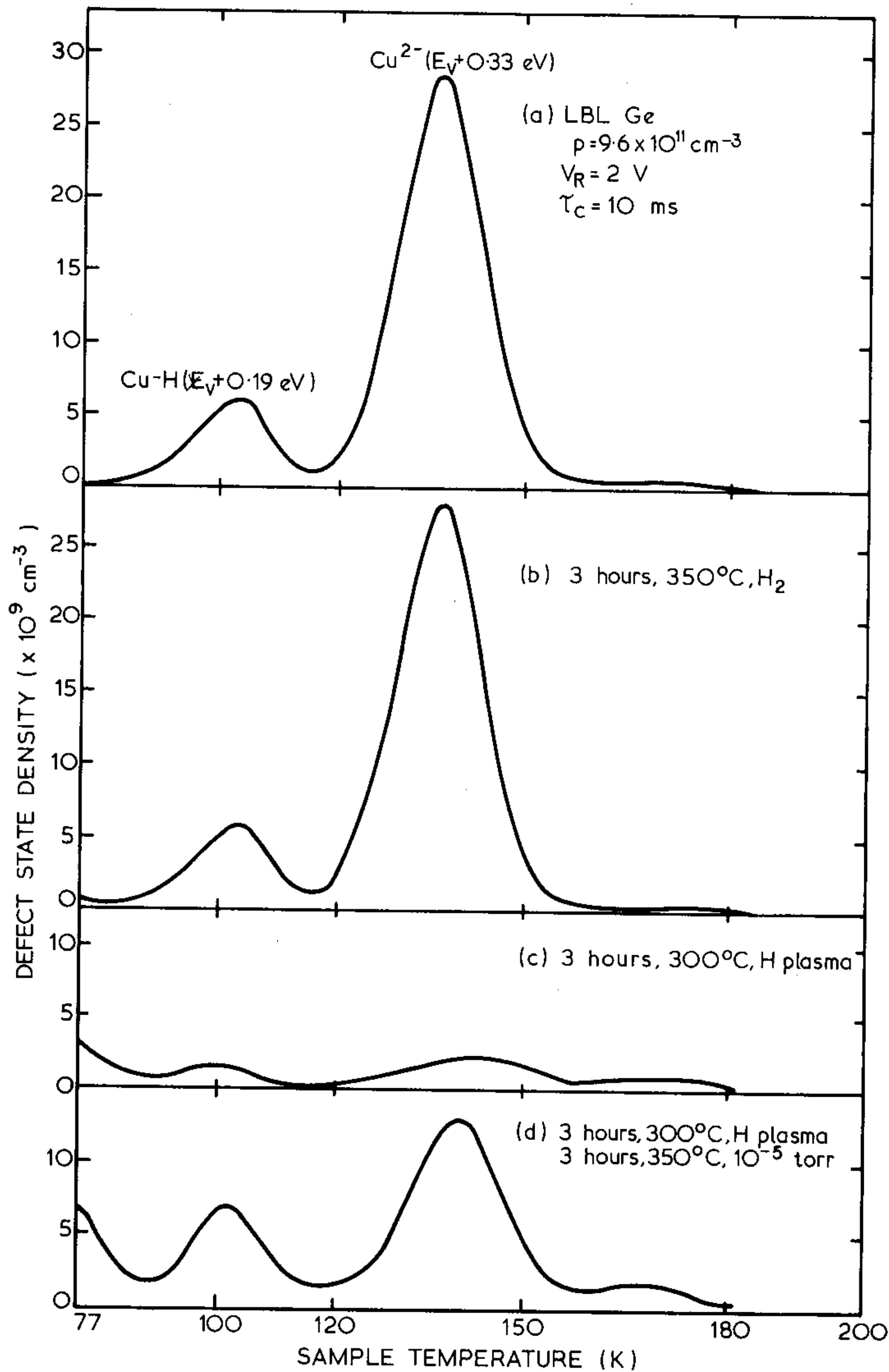

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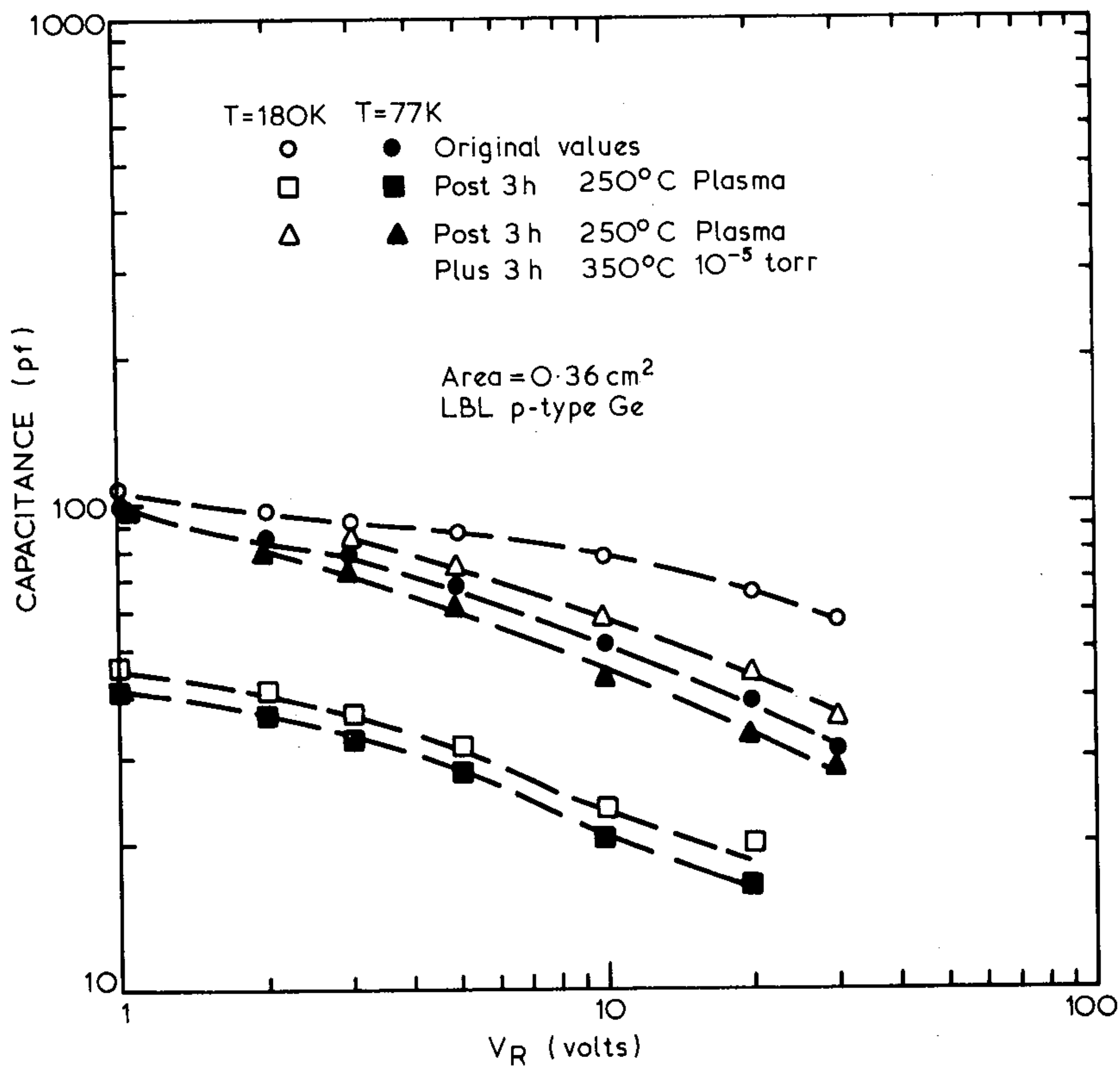

Figure 2 Capacitance-voltage measurements of a sample which has been hydrogenated for 3 hours at 250°C and subsequently annealed in vacuum, showing reduction in electrical activity of deep level defects with hydrogen incorporation

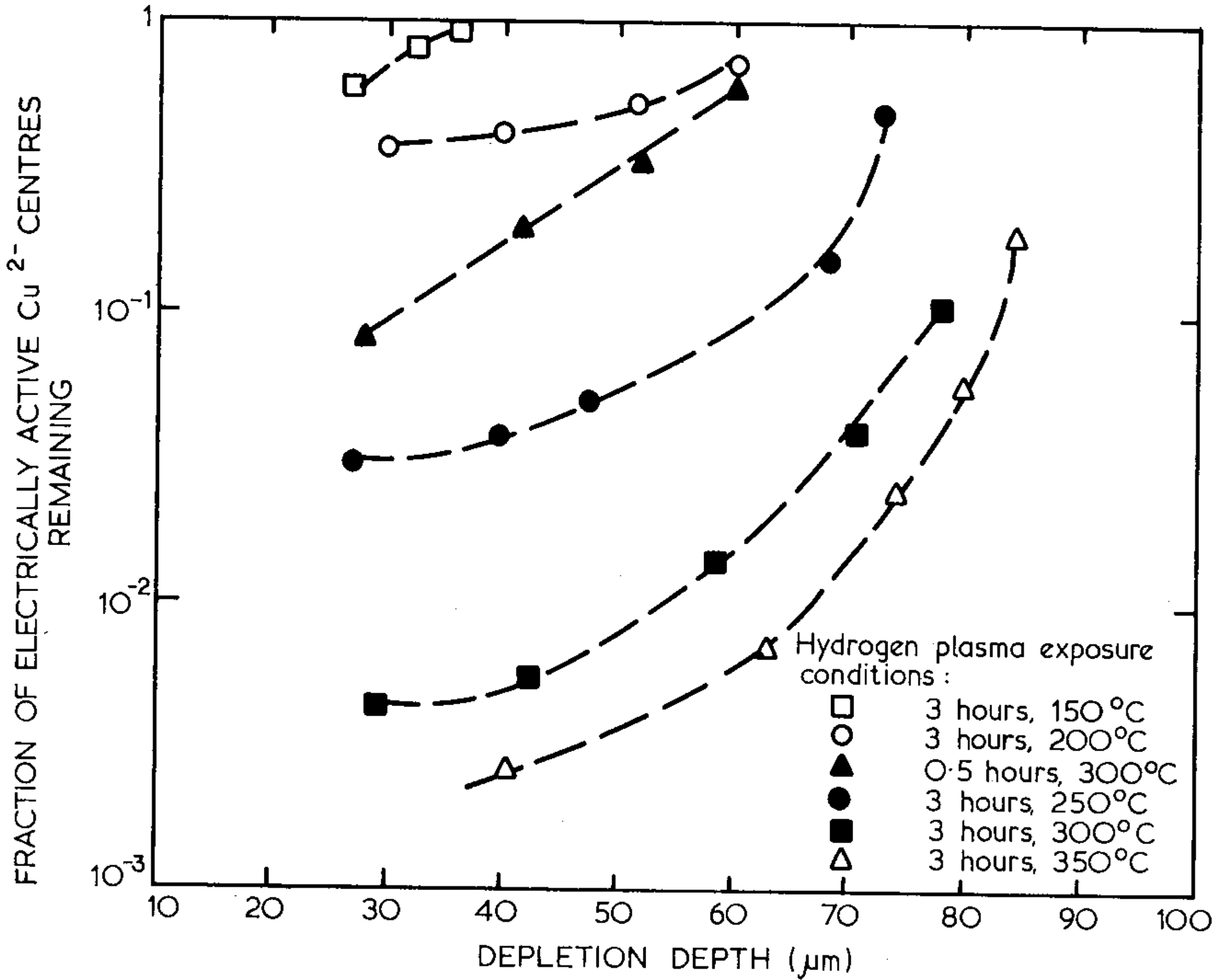

Figure 3 Concentration profile of the Cu^{2-} acceptor level as a function of the duration and temperature of the exposure to atomic hydrogen

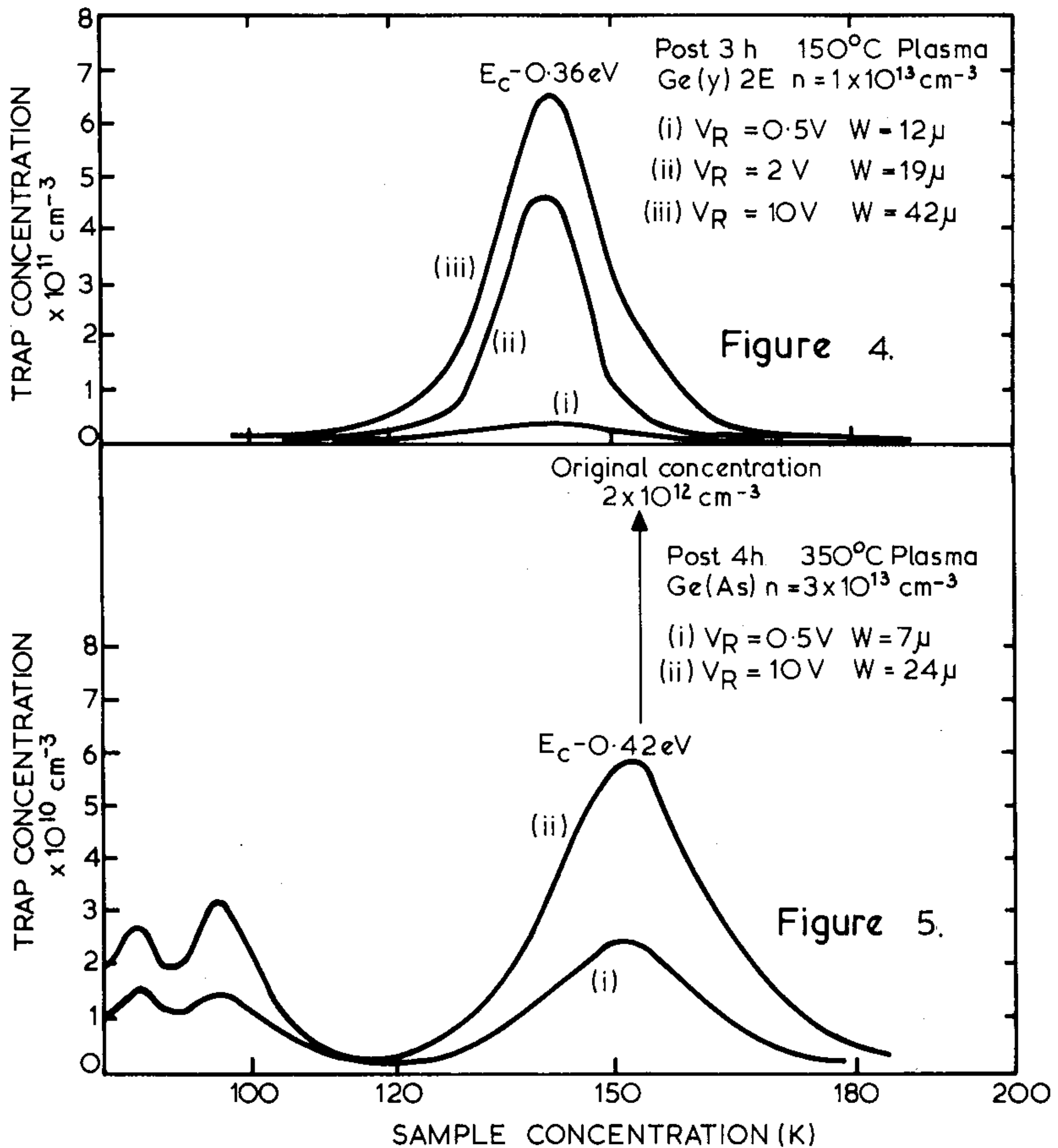

Figure 4 DLTS spectra for thermally stable deep donor level (E_c - 0.36 eV) in Hoboken n-type Ge, after plasma treatment for 3 hours at 150°C.

Figure 5 DLTS spectra for deep level defects in As-doped, γ-irradiated, n-type Ge, after plasma treatment for 4 hours at 350°C. The original density of the E_c - 0.42 eV level was 2 x 10^{12} cm^{-3} - this level does not begin to thermally anneal until ~700°C

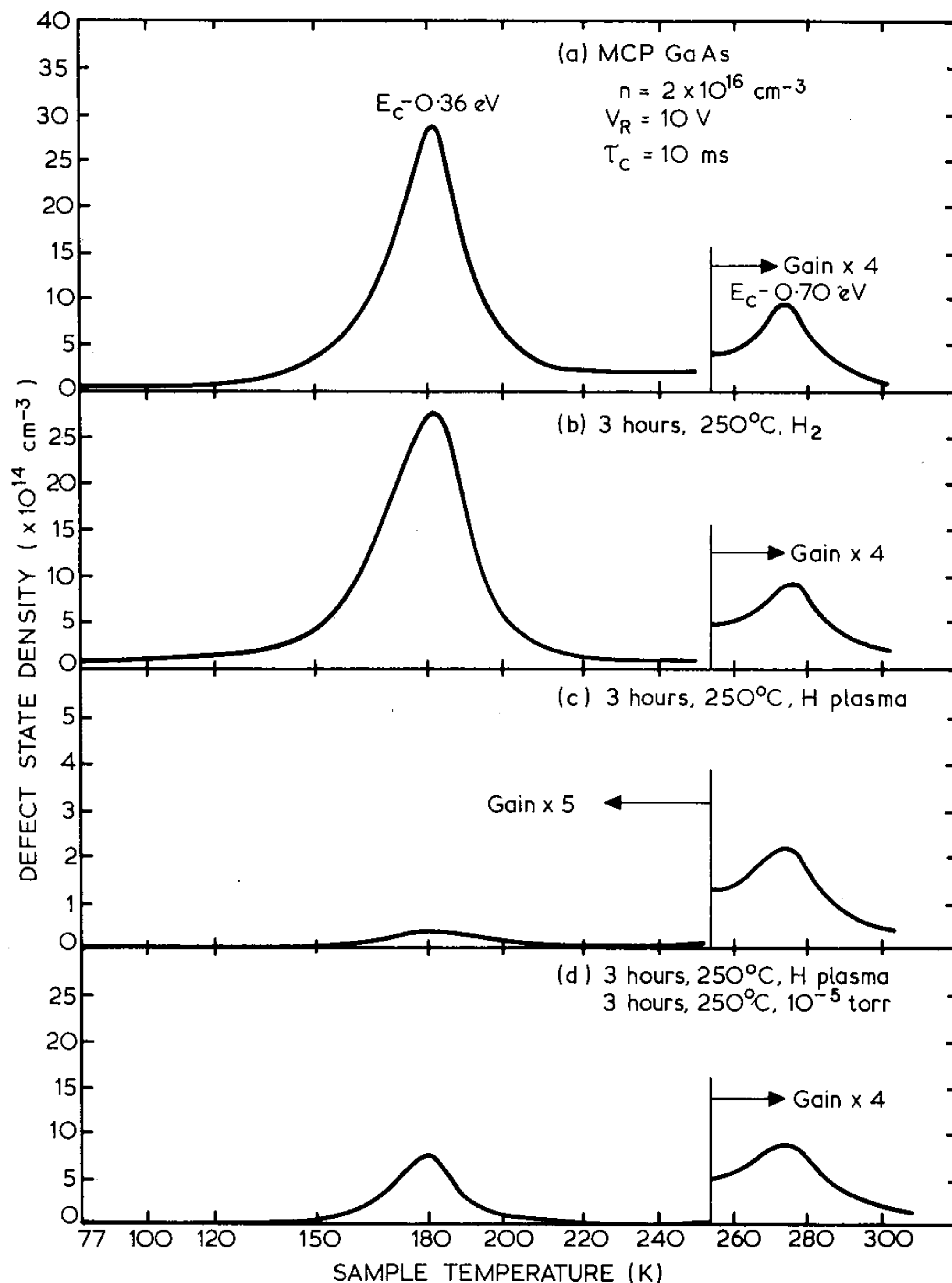

Figure 6 DLTS spectra recorded under the same conditions for (a) as processed MCP n-type GaAs showing two deep donor levels; (b) following a 3-hour 250°C anneal in H_2; (c) following a 3-hour, 250°C anneal in an H plasma; and (d) following plasma treatment and subsequent 3-hour 250°C anneal in vacuum

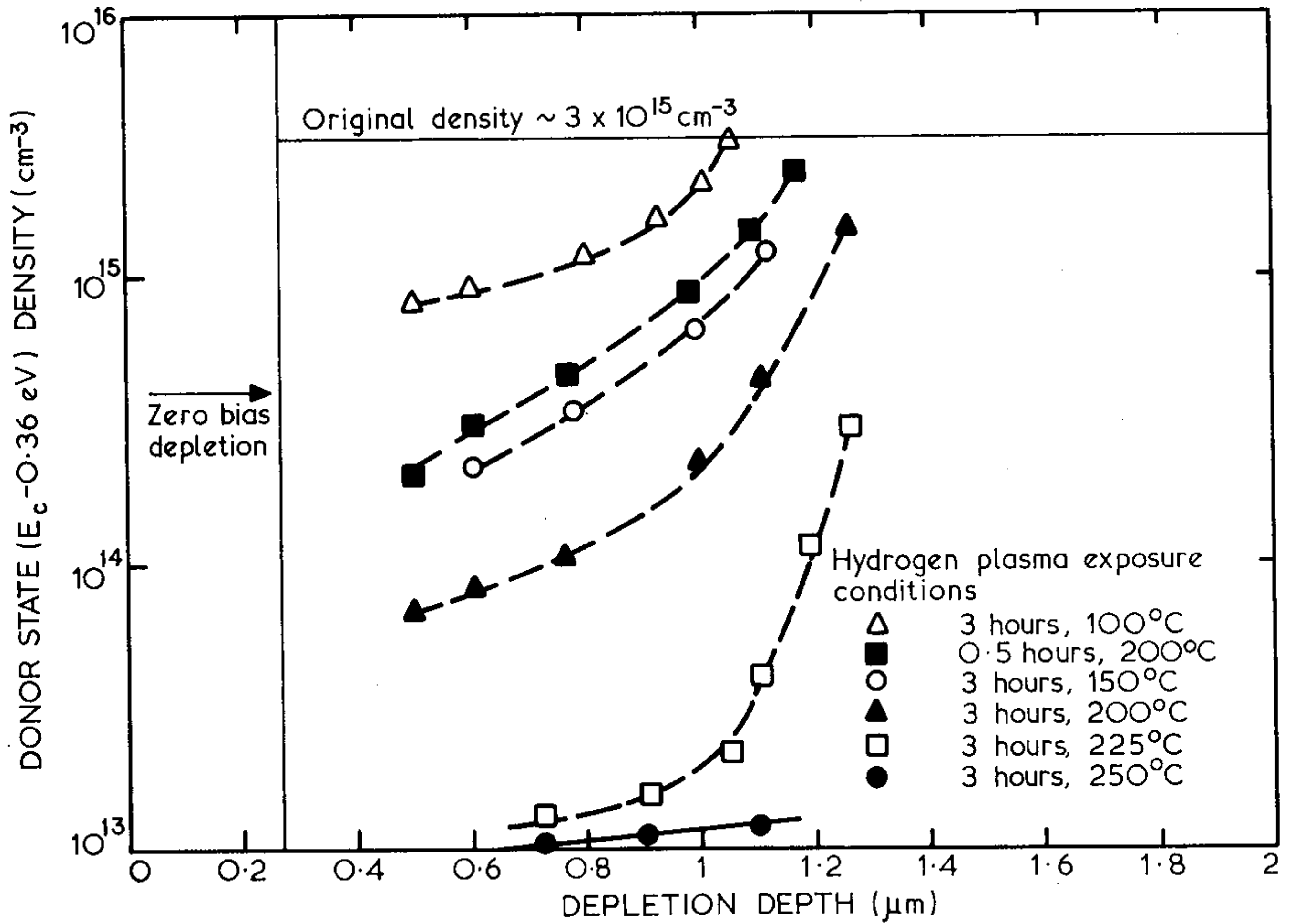

Figure 7 Concentration profile of the E_c - 0.36 eV centre as a function of the duration and temperature of the exposure to atomic hydrogen