dc-Hydrogen plasma induced defects in bulk *n*-Ge

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ABSTRACT

Bulk antimony doped germanium (*n*-Ge) has been exposed to a dc - hydrogen plasma. Capacitance-voltage depth profiles revealed extensive near surface passivation of the shallow donors as evidenced by ~ a 1.5 orders of magnitude reduction in the free carrier concentration up to depth of ~ 3.2 μm. DLTS and Laplace-DLTS revealed a prominent electron trap 0.30 eV below the conduction (E_C – 0.30 eV). The concentration of this trap increased with plasma exposure time. The depth profile for this defect suggested a uniform distribution up to 1.2 μm. Annealing studies show that this trap, attributed to a hydrogen-related complex, is stable up to 200 ^{o}C. Hole traps, or vacancy-antimony centers, common in this material after high energy particle irradiation, were not observed after plasma exposure, an indication that this process does not create Frenkel (V-I) pairs.

Keywords**:** Ge, hydrogen passivation, defects, DLTS, L-DLTS

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1. INTRODUCTION

Hydrogen passivation is an essential processing technique routinely used in the semiconductor device industry to de-activate shallow donors or acceptors, surface dangling bonds and even deep levels [1]. The passivation of dangling bonds by reaction with hydrogen atom can lead to lower leakage currents in *p-n* junctions, thereby improving for example, the efficiency of silicon solar cells [2]. One disadvantage of the hydrogenation process is that it can also introduce new electrically active hydrogen related complexes upon combining with native impurities in the material. The superior hole and electron mobility of Ge (over Si) and the potential it offers for more efficient and reliable complimentary metal-oxide semiconductor devices has sparked renewed interest in Ge thus motivating the study of defects in this material [3,4].

It is now well known that H^- is the stable species for all Fermi level positions in Ge [5]. Several authors have studied the incorporation of hydrogen in Ge by exposing the material to H-plasmas [2,5,6,11]. Weber et al [1] reported that the Ge surface constitutes an effective diffusion barrier (or binding center) for atomic hydrogen at elevated sample temperatures, consequently preventing a significant concentration of hydrogen into the bulk. Most work covers the passivation of metal and in particular transition metal related deep levels in Ge [2,6] at sample temperatures above 200 ^{o}C. Experimental proof of passivation of shallow donors has been reported by (amongst others) Bollmann et al. [5], but to the best of our knowledge, very little is known about dc H-plasma induced deep levels in Ge.

2. EXPERIMENTAL PROCEDURE

In this study, bulk grown (100) *n*-type Ge supplied by Umicore, doped with antimony (Sb) to a density of about 2 x 10^{15} cm^{-3} has been used. Prior to metallization, samples (1 cm x 0.5 cm) were degreased successively in trichloroethylene, acetone and methanol. Following this, the samples were etched in a mixture of H_2O_2:H_2O (1:5) for 1 minute before rinsing in de-ionized (DI) water and blown-dry in flowing N_2. Ohmic contacts were next fabricated by resistive evaporation of a 130 nm AuSb (0.6% Sb) layer onto the backside of the sample followed by annealing at 350 °C for 10 min in a 99.999 % argon (Ar) atmosphere. The samples were again chemically cleaned as

described above and then immediately exposed to a dc hydrogen plasma (described in detail in ref.[7]). During plasma exposure, the sample temperature was held at 100 ^{o}C while the chamber vacuum was maintained at 0.4 mbar. Next Schottky barrier diodes (SBDs) were fabricated on the front surface of the hydrogenated samples. This was preceded by a 2 min etch in $HF:HNO_3$ (1:1) to remove the heavily damaged near surface region for better contact quality. The etching rate was 58 nm/min, and a layer of 116 nm (0.12 μm) was removed after etching for 2 min. Immediately after etching Pd SBDs, 0.5 mm in diameter and 100 nm thick, were resistively deposited through a metal shadow mask. For experimental control purposes a sample was also exposed to molecular hydrogen in the plasma system (without forming a plasma) at 100 ^{o}C before SBD fabrication.

Room temperature (RT) current-voltage (*I-V*) and capacitance-voltage (*C-V*) measurements respectively were used to assess the SBD quality and monitor the free carrier concentration of the plasma exposed samples. Deep levels introduced by the hydrogenation process were characterized by deep level transient spectroscopy (DLTS) and Laplace-DLTS [8,9]. The '*signatures*' of the observed deep levels (i.e. energy position in band gap relative to the conduction band, E_T, and their apparent capture cross section, σ_a), were determined from Arrhenius plots of $ln(T^2/e)$ vs. 1000/T. Here, e represents the electron emission rate, and T the measurement temperature in Kelvin. In addition, the thermal behaviour of the defect introduced by the H-plasma was studied by annealing the samples isochronally (10 min) between RT and 300 °C in an Ar ambient.

3. RESULTS AND DISCUSSION

3.1. Hydrogen passivation of shallow donors

Fig. 1 shows free carrier concentrations (obtained from $1/C^2$ *vs* V profiles) as function of H-plasma exposure (hydrogenation) time recorded at a depth of 1.4 μm prior and after hydrogen passivation of the bulk *n*- Ge. The exposure periods were 0 (reference), 5, 15 and 25 min while the sample temperature was maintained at 100 ^{o}C. Fig. 2 shows *C-V* depth profiles of (a) the reference and (b) the H-plasma exposed (25 min) samples. These profiles clearly show that the free carrier density, following

exposure to the H-plasma for 25 min, is reduced by ~ 1.5 orders of magnitude. This can be explained by passivation of shallow donors within this region when atomic hydrogen combines with donor (Sb) atoms forming neutral H-Sb complexes. This explanation is supported by the fact that annealing (as discussed below) recovers/ partially recovers the free carrier concentration of the passivated sample. This is contrary to what is observed with MeV proton bombardment for which Frankel pairs are responsible for a decrease in the free carrier concentration. Annealing the passivated sample (a) between RT and 175 ^{o}C did not result in a noticeable change in the *C-V* depth profiles. However, annealing between 200 ^{o}C - 300 ^{o}C resulted in a progressive increase in the free carrier concentration, a clear indication of the thermal reactivation of the H-complexed shallow donors.

3.2. Hydrogen plasma induced deep levels

In addition to the shallow level passivation discussed in section 3.1, H-plasma exposure also introduced a single prominent electron trap with a concentration that increases with the plasma exposure time. Fig. 3 shows DLTS spectra for (a) the reference and (b-d) the H-plasma exposed samples (5, 15 and 25 min respectively). (It is instructive to note that the starting material used, (i.e. not being exposed to molecular hydrogen or H-plasma) were defect free as pointed out in ref. [10]). Clearly the reference sample in this study (exposed to molecular hydrogen at 100 ^{o}C spectrum (a)) also does not contain any deep levels within the detection limit of our system ($\sim 10^{11}$ cm^{-3}). An electron trap E(0.31) with similar signature was observed in similar samples after high energy (MeV) proton irradiation [10]. Fig. 4 depicts Arrhenius plots for the electron trap E(0.30) observed in this study and that reported by C. Nyamhere et al. [10]. The electron trap E(0.30) detected in this study after H-plasma treatment has an activation energy of E_C - 0.30 eV and an apparent capture cross-section of 2.2 x 10^{-14} cm^{2}. Clearly the respective trap signatures are very similar. This trap is tentatively attributed to an electrically active defect complex involving H and other impurities in the substrate. Lauwaert et al. [11] observed a single electron trap level at E_C – 0.237 eV in *n*- Ge doped to 8 x 10^{14} cm^{-3} (dopant not specified), after passivation with H-plasma at a vacuum pressure of 6.10 Pa (0.061 mbar), sample temperature of 150 ^{o}C and exposure time of 2.5 hrs. The difference in trap activation energy suggests that a different complex is formed as a result of possibly different dopants, sample temperature and hydrogenation conditions (Fig. 4).

Fig. 5 shows the concentration depth profile of the H-plasma related electron trap, E(0.30) observed in this study. The trap concentration (assuming a constant uncompensated doping concentration from 0.4 μm up to 1.3 μm) is constant at ~ 3-5 × 10^{12} cm^{-3} within the region profiled, thus indicating that the trap is a consequence of the bombardment of the near-surface region with the hydrogen-plasma species. It should be noted that although a reverse bias of -5 V has been used, the defect concentration depth profile method used here (fixed bias-variable pulse method with the transition region correction [12]) takes into account the band bending and as such the DLTS measurement does not probe the region at the depletion region edge, but a region a distance (transition region) λ shallower, given by

$$\lambda = \sqrt{\frac{2\varepsilon_{S}(E_F - E_T)}{qN_d}} = 1.07\ \mu\text{m}, \qquad (1)$$

where ε_s is semiconductor permittivity, E_F is the Fermi level, q is the electron charge and N_d is the uncompensated doping concentration. In addition to the transition region correction, poor signal/noise ratios for DLTS signals recorded after smaller pulses (deeper regions) resulted in unreliable data points, hence larger pulses were considered translating to shallower profiling than expected for such a reverse bias.

The annealing behaviour of E(0.30) shows that this defect is stable up to 200 °C, and trap concentration is inversely correlated to the free carrier concentration upon reactivation (Fig. 2). This supports the notion that the defect may be related to a H complex and it is completely removed after annealing at 300 °C (Fig. 6).

4. SUMMARY

The hydrogen plasma performed at sample temperature of 100 °C and for different exposure time resulted in successful passivation of shallow donors in Ge. The density of the passivated donors increased with exposure time. The passivation process introduced an electron trap E(0.30). This defect is probably related to a complex involving H, but further to work clarify its origin is required. Increasing the exposure time resulted in an increase of the defect concentration. Annealing studies shows that this complex is stable up to 200 °C, which correlates well with the temperature at

which the shallow donors start to be re-activated. Finally, the thermal reactivation of the passivated free carriers is inversely correlated to the defect concentration following annealing.

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Fig. 1 Free carrier concentration versus plasma exposure time recorded at a depth of 1.4 μm.

Fig. 2 (color on line) *C*-*V* depth profiles of (a) the reference and (b) the H-plasma exposed (25 min) *n*-Ge samples. Thermal reactivation of the passivated donors is clearly evident following isochronal annealing between 200 ^{o}C and 300 ^{o}C.

Fig. 3 shows DLTS spectra (a) of the reference and (b-d), after H-plasma exposure for 5, 15 and 25 min respectively. The spectra were recorded at a quiescent reverse bias of -2 V and a pulse height of 2 V. The pulse width and rate window were 1 ms and 80 s^{-1}, respectively.

Fig. 4 Arrhenius plots of electron traps in *n*-type Ge after H passivation (closed circles) and after MeV proton irradiation (open triangles).

Fig. 5 The concentration depth profile of the electron trap E(0.30) after hydrogen passivation for a period of 25 minutes. The spectra were recorded at quiescent reverse bias of -5V, a varying pulse height (fixed bias-variable pulse method ref.[12]) and pulse width of 1 ms.

Fig. 6 The annealing behaviour of E(0.30) introduced in *n*-Ge after hydrogen passivation recorded between RT and 300 ^{o}C.

Fig. 1

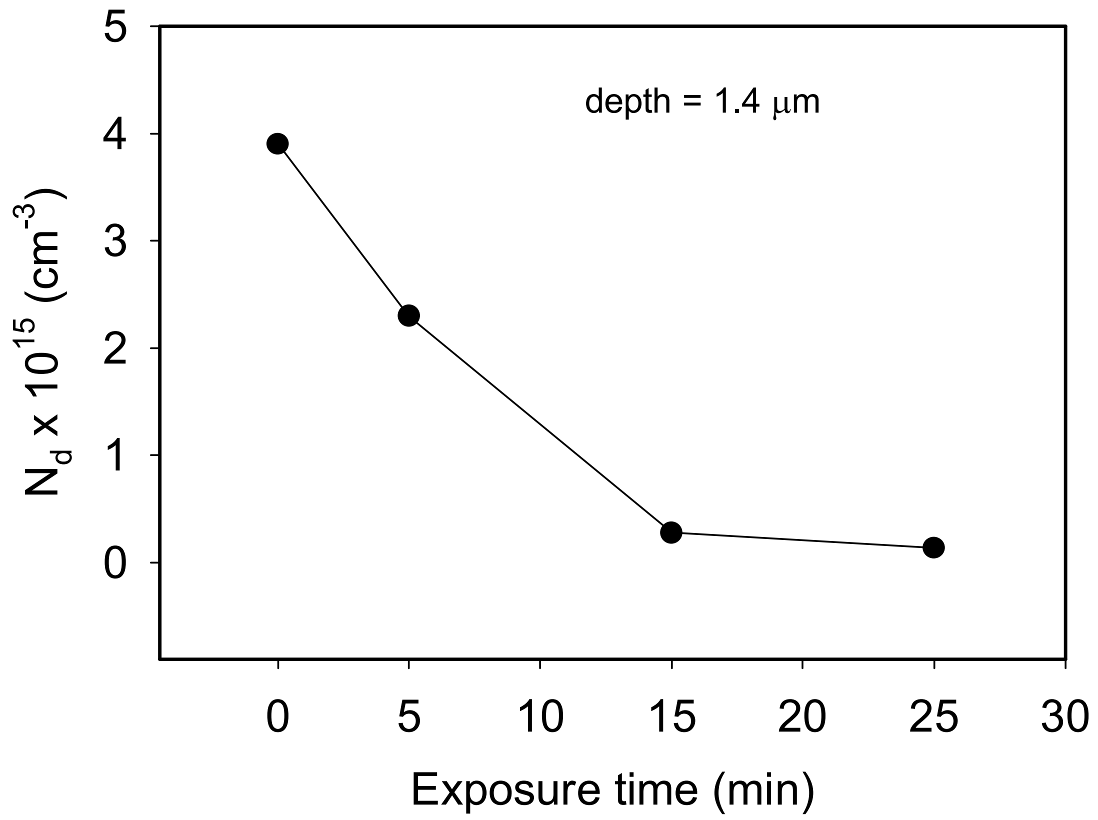

Fig. 2

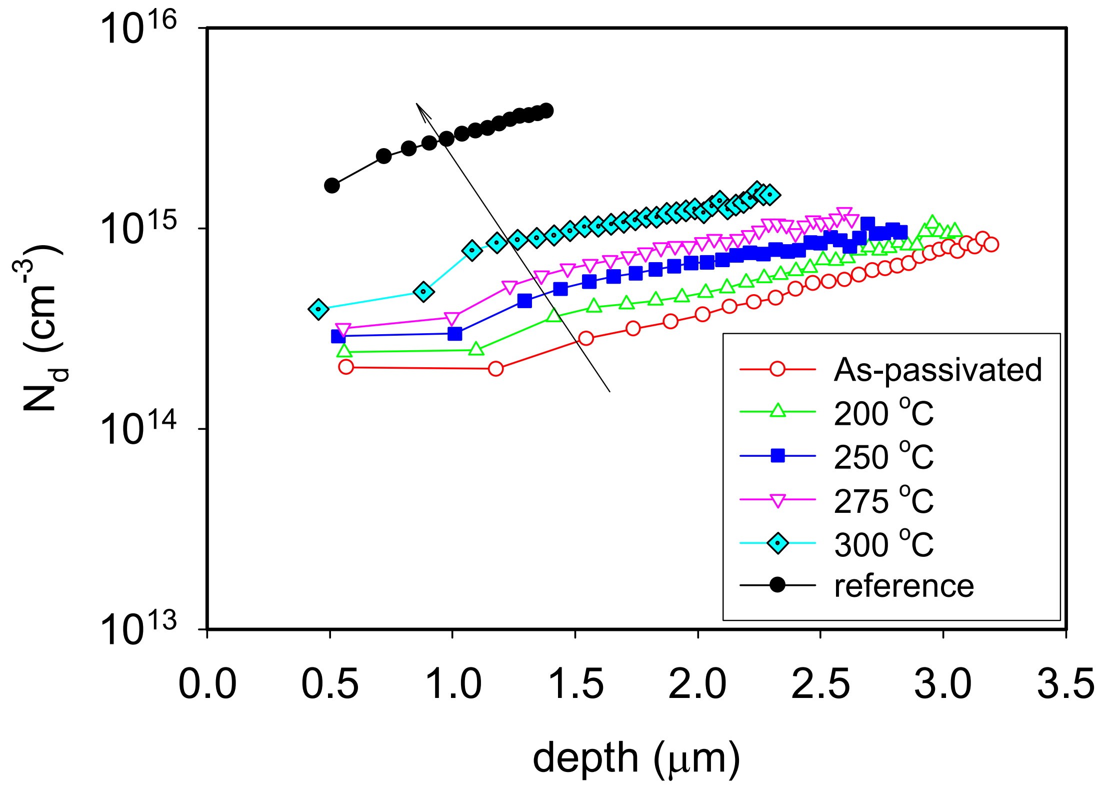

Fig. 3

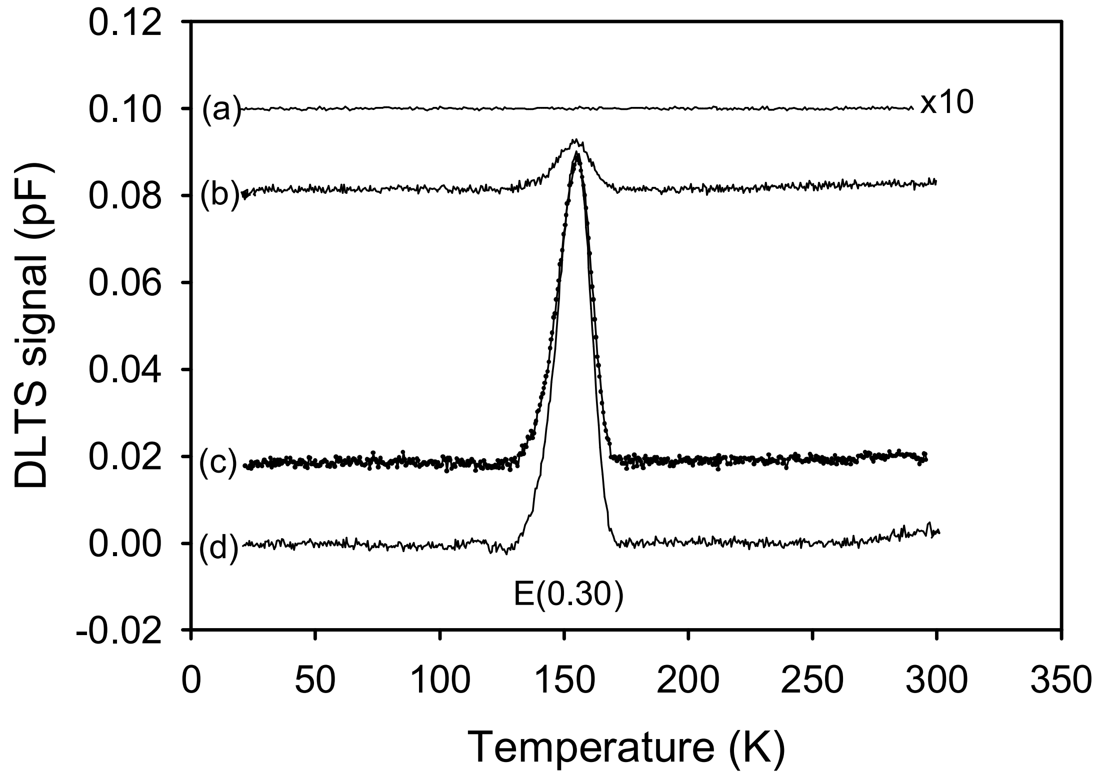

Fig. 4

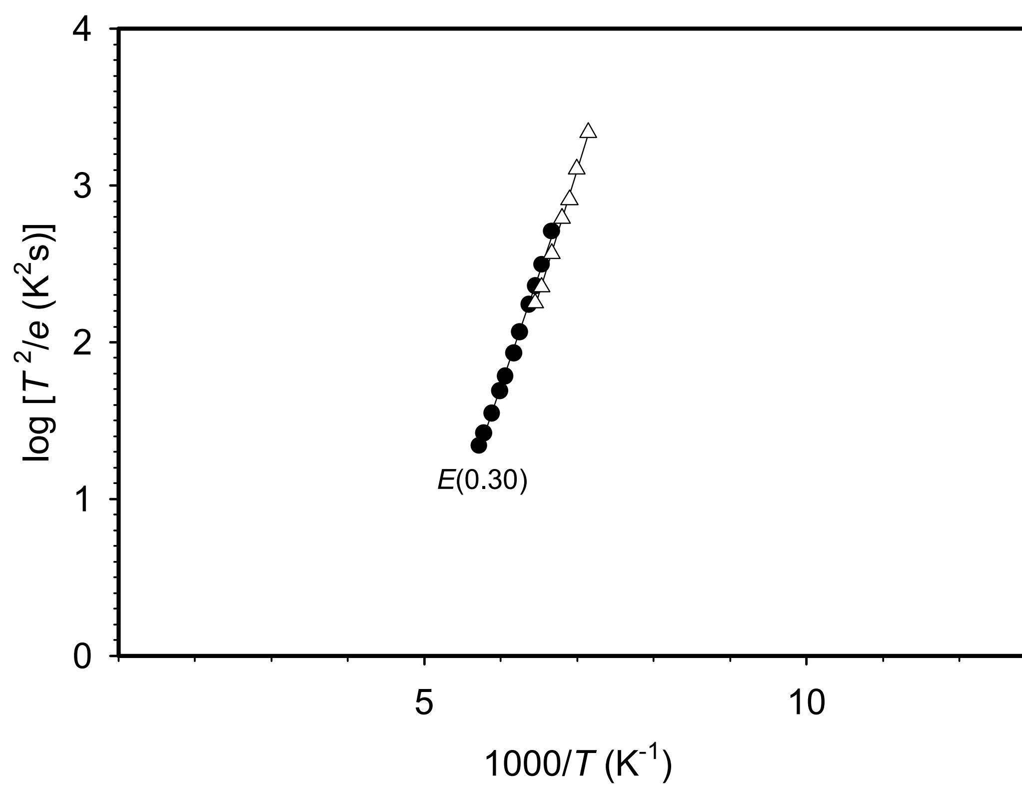

Fig. 5

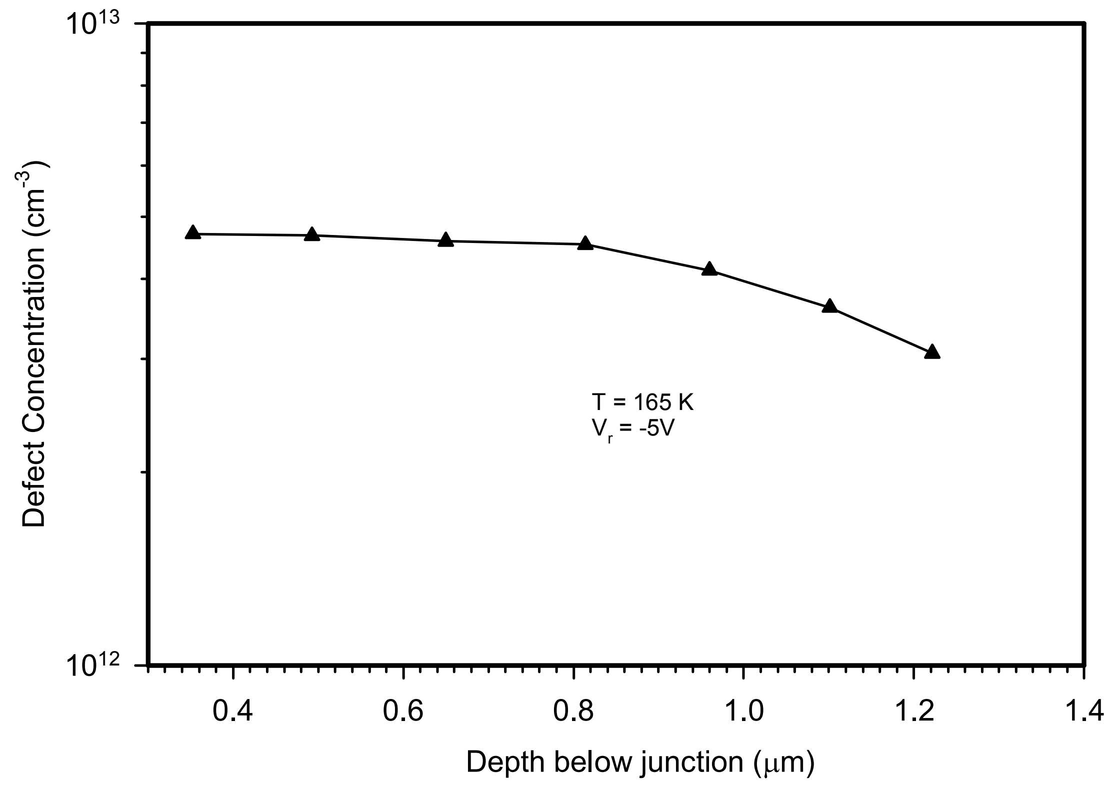

Fig. 6