EFFECTS OF PLASMA HYDROGENATION ON TRAPPING PROPERTIES OF

DISLOCATIONS IN HETEROEPITAXIAL InP/GaAs[1]

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ABSTRACT

In previous work, we have demonstrated the effectiveness of a post-growth hydrogen plasma treatment for passivating the electrical activity of dislocations in metalorganic chemical vapor deposition (MOCVD) grown InP on GaAs substrates by a more than two order of magnitude reduction in deep level concentration and an improvement in reverse bias leakage current by a factor of ~ 20 (refs. 1-2). These results make plasma hydrogenation an extremely promising technique for achieving high efficiency large area and light weight heteroepitaxial InP solar cells for space applications. In this work we investigate the carrier trapping process by dislocations in heteroepitaxial InP/GaAs and the role of hydrogen passivation on this process. It is shown that the charge trapping kinetics of dislocations after hydrogen passivation are significantly altered, approaching point defect-like behavior consistent with a transformation from a high concentration of dislocation-related defect bands within the InP bandgap to a low concentration of individual deep levels after hydrogen passivation. It is further shown that the "apparent" activation energies of dislocation related deep levels, before and after passivation, reduce by ~ 70 meV as DLTS fill pulse times are increased from 1 usec. to 1 msec. A model is proposed which explains these effects based on a reduction of Coulombic interaction between individual core sites along the dislocation cores by hydrogen incorporation. Knowledge of the trapping properties in these specific structures is important to develop optimum, low loss heteroepitaxial InP cells.

INTRODUCTION

Dislocations within InP layers grown on lattice mismatched substrates such as GaAs, Si and Ge are currently a major limitation for the development of efficient heteroepitaxial InP solar cells for space applications. The ~ 8% mismatch in lattice constant for InP/Si, and 4% for both InP/Ge and InP/GaAs, typically result in threading dislocation densities in the range $1\text{-}10\times10^8$ cm^{-2} in the InP layers which has severely reduced heteroepitaxial InP cell efficiencies thus far (ref. 3). This has prompted investigations of a number of approaches to reduce threading dislocation density toward 1×10^5 cm^{-2}, the theoretically predicted value necessary to achieve efficiencies comparable to homoepitaxial InP/InP (ref.3). These approaches include the use of compositionally graded buffer layers, thermally cycled growth and hydrogen passivation (refs. 1-5).

For the case of hydrogen passivation, where the focus is on reducing the electrical activity of dislocations rather than total dislocation concentration, it has been shown that exposure of p-InP grown on GaAs substrates to a hydrogen plasma at 250 °C reduces the dislocation related deep level concentration from ~ 6×10^{14} cm^{-3} to ~ 3×10^{12} cm^{-3} in the InP layer (ref. 1). This passivation was found to be stable up to ~ 550 °C, which combined with dopant reactivation occurring at 380 °C, opens a 170 °C post-passivation processing window for cell completion. Furthermore, it was shown that reverse leakage currents of heteroepitaxial InP diodes on GaAs were significantly improved as the result of dislocation passivation. These results are summarized in Figures 1 and 2.

In addition to reducing the concentration of deep levels resulting from dislocations, hydrogen incorporation is found to change the mechanisms of the actual carrier trapping process. Knowledge of the dislocation trapping properties is critical to understand current transport characteristics of heteroepitaxial cells and must be accounted for in heteroepitaxy-specific cell design optimization. In this paper we present a study of the charge trapping properties of dislocations in p-type InP grown by MOCVD on GaAs substrates, both prior to and after hydrogen passivation.

EXPERIMENTAL

InP was grown on (100) GaAs substrates by low pressure MOCVD. Growth details have been reported elsewhere (ref. 1). The InP structure consisted of a 2 μm thick layer of Zn doped p-type (1×10^{17} cm^{-3}) InP grown on a 0.5 μm thick n$^+$ InP layer on n$^+$ GaAs substrates. Ohmic contacts were formed by electron beam evaporation and patterning of Au/Zn/Au and Ni/Ge/Au on the p-type InP and n-type GaAs substrate, respectively, followed by a 380° C anneal in N$_2$. This device structure, shown in Figure 3, allows us to probe the depletion region as measured from the buried junction and up toward the InP surface.

Hydrogenation was performed in a Technics Planar Etch II 30 kHz parallel plate plasma reactor. Hydrogen exposure was performed using a 30 sccm flow rate of semiconductor grade H$_2$, chamber pressure of 530 mTorr, power density of 0.08 W/cm^2 and a substrate temperature of 250° C. Hydrogen exposure time was either 1.5 or 2 hours, as noted. Immediately prior to hydrogen exposure, all samples were capped with a thin, hydrogen-permeable, ~ 20 nm layer of SiN$_x$ to prevent surface degradation by preferential loss of phosphorous during hydrogenation. The nitride layer was etched off in dilute HF before metallization. DLTS measurements were performed using a Biorad DL4602 DLTS spectrometer, respectively based on the double boxcar data acquisition method. Fill pulse times were controlled using the Biorad pulse timing circuit and by an external pulse generator.

Note that all data of hydrogenated samples discussed in this paper received a post hydrogenation dopant reactivation anneal for 380 °C for 5 minutes.

RESULTS AND DISCUSSION

Figure 4 shows the DLTS spectra for non-hydrogenated heteroepitaxial InP measured at a rate window of 1000/sec. as a function of fill pulse time. The fill pulse time dependence of the three main peaks (T1, T2 and T3) is more quantitatively depicted in Figure 5a (before hydrogenation) and 5b (after hydrogenation) where it is seen that the peak height variation of T1 and T2 display a linear relationship with the natural logarithm of the fill pulse time. Such behavior is consistent with earlier reports for charge capture by extended defects and dislocations in other semiconductors which has been described by a rate equation given as (ref. 6)

$$dp_T/dt = [(c_p + e_n)(N_T - p_T(t)) - (c_n + e_p)p_T(t)]\exp(-q\phi(t)/kT)$$ (1)

where $c_{n,p}$ are capture rates for electrons and holes, $e_{n,p}$ are emission rates for electrons and holes, p_T is the concentration of traps filled with holes, N_T is the total trap concentration, and $\phi(t)$ is a time dependent potential barrier associated with the charging of a dislocation. Note that this differs from the usual point defect rate equation only by the presence of the exponential term which acts to slow the trap filling rate. The solution of this equation, after some simplification and in terms of the trap fill pulse time, t_p, used in the DLTS experiment is given by (ref. 6)

$$p_T(t_p) = \sigma_p<v_p>n\tau N_T \ln[t_p/\tau]$$ (2)

The term τ in equation (2) is proportional to the height of this potential barrier and p_T is proportional to $\Delta C/C$ as given in Figure 5. Note that in each of these plots of Figure 5, T1 and T2 follow the logarithmic behavior

and extended fill pulse time dependence predicted for dislocations, whereas T3 follows the usual point defect behavior. In fact, we have earlier shown that T3 was indeed associated with a point defect since it was the only level evident in the DLTS spectra of homoepitaxial InP/InP structures (ref. 7). By comparing Figures 5a and 5b, it can be seen that hydrogen passivation results in a significant change in the slope of the plotted data. Calculations have shown that the slope for the T1 and T2 curves reduce by approximately two orders of magnitude after hydrogenation, indicating that the trap state density is decreased as expected, and that the barrier to carrier trapping, $\phi(t)$, has been lowered.

While the logarithmic capture kinetics is one characteristic of the unusual trapping properties of dislocations in heteroepitaxial InP, it is also clear from Figure 4 that T1 and T2 broaden on the low temperature side of the DLTS peaks as the fill pulse time is increased, resulting in a shift toward lower temperatures of the peak maximum with fill pulse time. This is shown more quantitatively for T2 in Figure 6 where the FWHM/T_p is plotted against the fill pulse time (T_p is the temperature at which the DLTS peak is maximum). It can be shown that for a single deep level, FWHM/T_p = 0.104 for a rate window of 1000/sec., which should not vary with fill pulse time. As seen in the figure, T2 is clearly broadened compared to this value and furthermore, varies with fill pulse time until it saturates at $t_p \sim 0.1$ msec. This behavior can be understood if one first considers that dislocations are generally thought to cause a band of deep levels, rather than non-interacting isolated levels, due to wavefunction overlap of closely spaced dislocation core states. In this case, only the lower energy states within the band are filled for very short fill pulse times. As fill pulse time increases, higher energy states can trap carriers, eventually saturating as the band becomes filled. It can be shown that the higher energy states for holes (this corresponds to states closer to the valence band), which result in lower activation energies (E_T -E_v), will always contribute DLTS peaks at lower temperatures for the same rate window and cross section, compared to lower energy states (higher activation energies). This would explain why the DLTS peaks broaden only on their low temperature sides. It should be noted here that a similar analysis was performed for T1. A complete analysis will be presented elsewhere.

Figure 6 also includes FWHM/T_p data for hydrogen passivated samples. Note that in comparison to non-hydrogenated data, the FWHM/T_p characteristic of peak T2 after hydrogen passivation is much closer to that of an ideal point defect, although it is still somewhat broadened. This is likely the result of a reduction in the active core site density which causes an increase in the average active core site spacing and a change in the dislocation density of states.

The result of the peak broadening and shifting for DLTS interpretation is most striking in Figure 7, which shows the measured trap activation energy for T1, T2, and T3 as a function of fill pulse time following the usual Arrhenius method. First consider the non-hydrogenated data. As can be seen, the measured activation energy shifts by approximately 80 meV for T1, from $\sim$ 880 eV for a 1usec. fill pulse time, to $\sim$ 800 eV for a 10 msec. fill pulse time. T2 shows a shift of similar magnitude. In contrast, the point defect level, T3, shows no such dependence, as would be expected. For the complicated case of dislocations, the Arrhenius method for DLTS activation energy actually yields the *weighted average energy of the filled states within the dislocation energy band that contribute to carrier emission*. For short fill pulse times, only those states farthest from the valence band are filled with holes, resulting in larger activation energies. One would therefore expect a more "point defect-like" behavior due to reduced dislocation charging. This is corroborated by Figure 6 which shows less peak broadening for short fill pulse times. For longer fill pulse times, the band fills downward with higher energy holes (toward the valence band edge). Therefore the average energy of the re-emitted holes is higher and the measured average activation energy decreases, as observed. Eventually, for longer fill pulse times, the band will saturate with trapped holes. At this point, the measured activation energy is indicative of the weighted average over the entire band. Note that the variation of activation energy in Figure 7 is completely consistent with the FWHM/T_p variation shown in Figure 6. These results suggest that care should be taken when comparing DLTS measured activation energies for dislocations, with particular attention to the fill pulse time used in the experiment.

The effect of hydrogen passivation on the activation energy behavior is also shown in Figure 7 for each DLTS peak. Again, negligible change in activation energy is observed for the point defect level, T3,

while a significant change of activation energy with fill pulse time is still evident for both T1 and T2. However, from the figure it is clear that the activation energies of T1 and T2 are consistently higher for all fill pulse times after hydrogenation. It should be noted that the shape of the activation energy dependence on fill pulse time also changes after hydrogen passivation. This is likely a result of reduced density of states at certain energies due to passivation, which allows a faster change, or response, to fill pulse time. This suggest that such a plot of activation energy versus fill pulse time may provide information about the actual shape of the dislocation density of states. This is currently being looked at in more detail.

CONCLUSIONS

Hydrogen passivation by plasma hydrogenation has been shown to be effective in reducing the electrical activity of dislocations in p-type InP grown on GaAs substrates. Deep level concentrations were reduced by more than 2 orders of magnitude and diode leakage currents were suppressed. These beneficial effects were found to be stable up to a post hydrogenation annealing temperature of 550 °C. Detailed analysis of the dislocation trapping kinetics prior to hydrogenation showed the expected logarithmic trapping kinetics as reported for dislocations in other materials. Furthermore, it was shown that this was related to the observed DLTS peak broadening toward lower temperatures with fill pulse time and a large dependence of measured trap activation energy on fill pulse time. It was found that hydrogen passivation significantly altered the fundamental trapping properties of the dislocations, resulting in a decrease in the broadening of the dislocation related DLTS peaks in addition to a shift in the average energy of the dislocation density of states away from the valence band. These effects suggest that hydrogen passivation reduces the interaction between adjacent dislocation core sites and results in a trapping behavior that approaches that expected for point defects.

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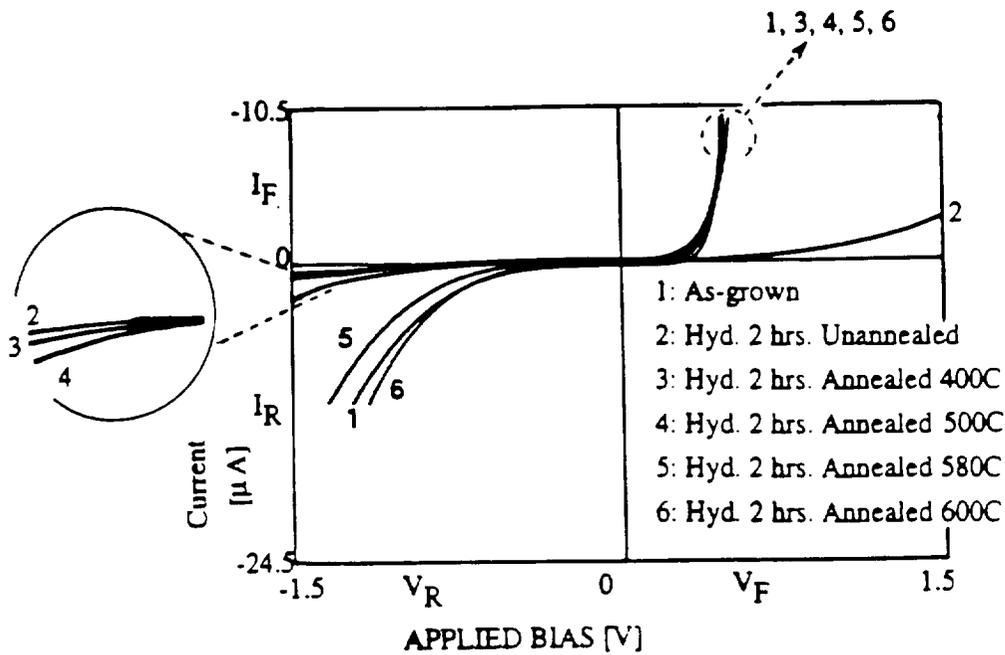
Figure 1. Current-voltage characteristics of p-InP/n⁺-InP diode grown on GaAs, measured before and after hydrogenation and after various post-hydrogenation anneals at the temperatures indicated.
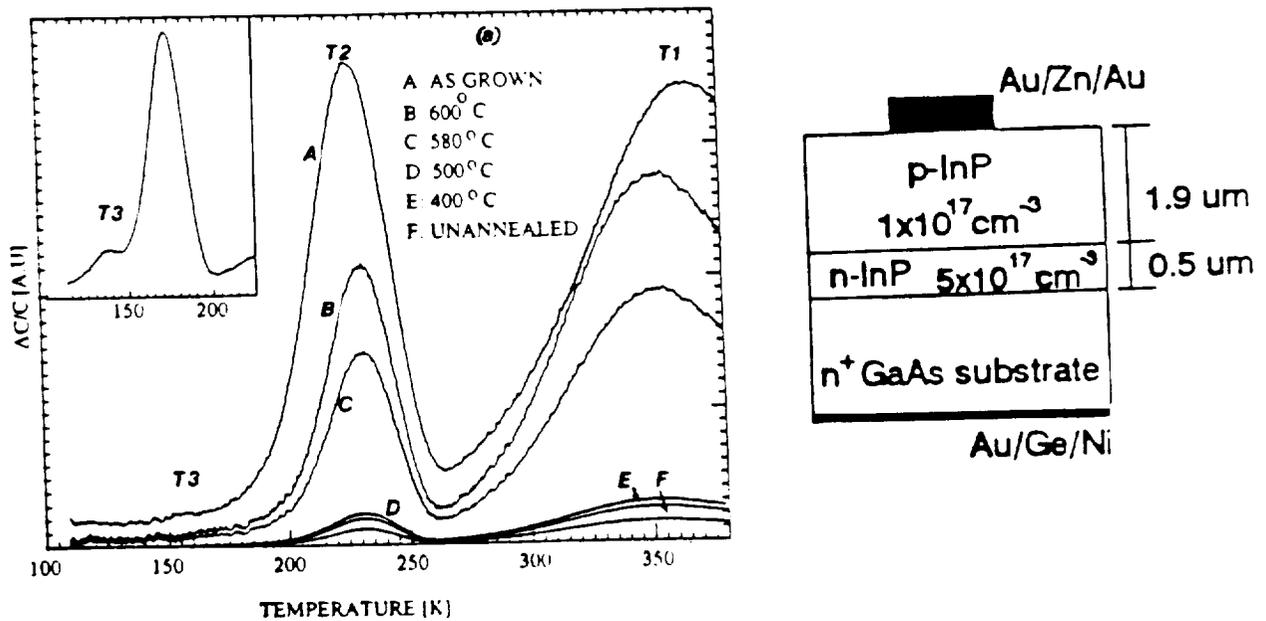
Figure 2. Effect of hydrogenation and post-hydrogen anneals on DLTS spectra for InP/GaAs, measured at a rate window of 1000/sec. The inset measured at 50/sec rate window, clearly shows trap T3, which is prominent at higher rate windows.
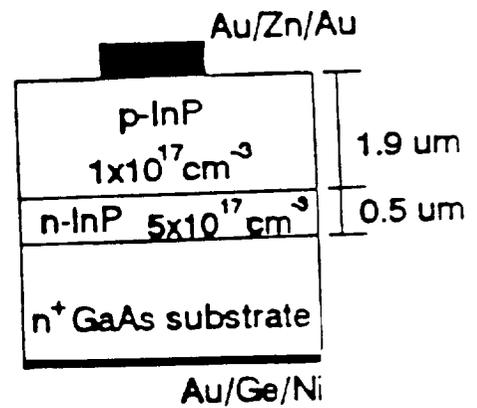
Figure 3. Device structure used for this study.

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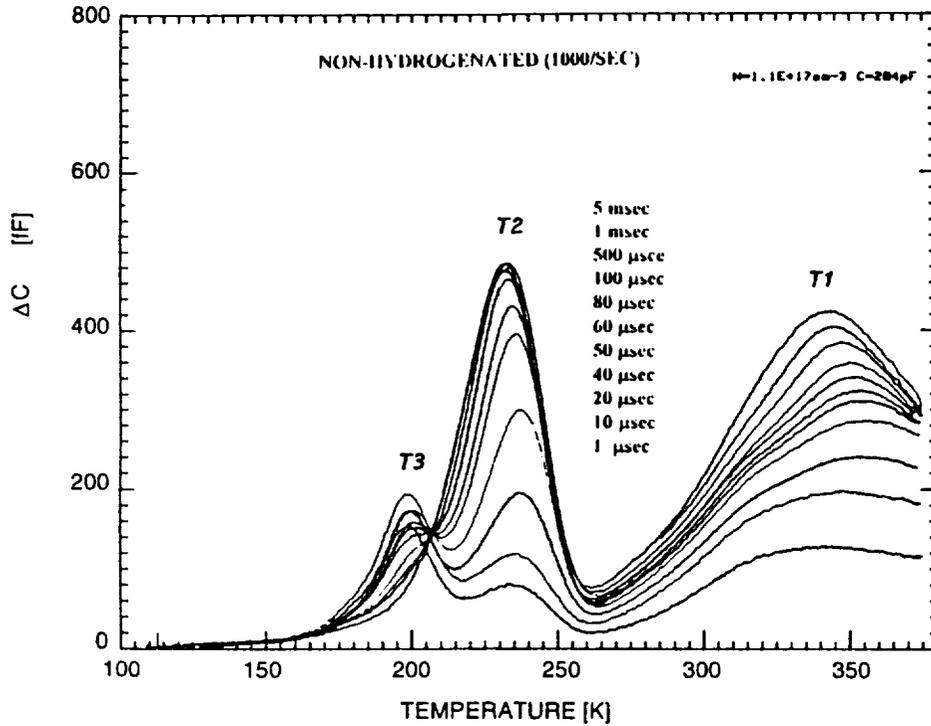
Figure 4. DLTS spectra measured at 1000/sec. rate window for the different fill pulse times as shown.
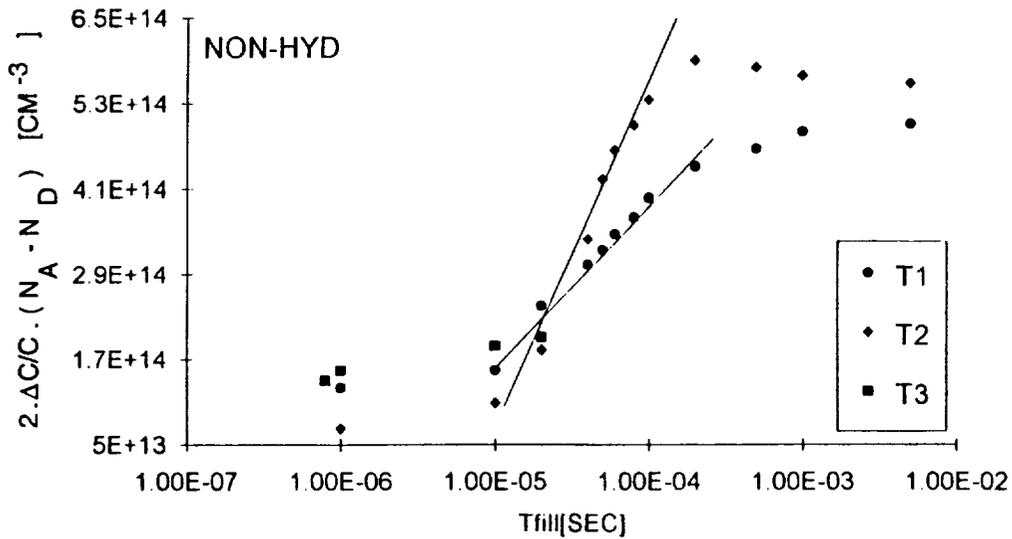
Figure 5(a). Capture characteristics for traps T1, T2 and T3 before hydrogenation. T1 and T2 exhibit extended dependence on fill pulse time that is characteristic of dislocations and follows eqn. (2).

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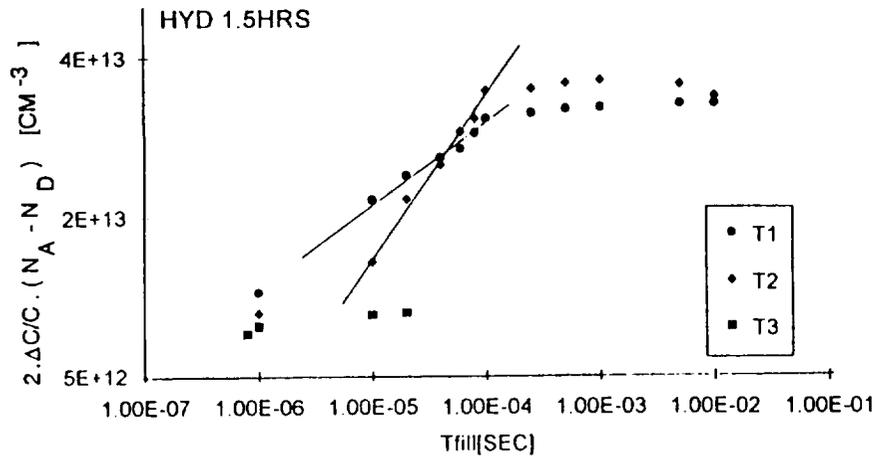
Figure 5(b). Capture characteristics for traps T1, T2 and T3 after hydrogenation. Note the reduction in slope for T1 and T2 compared to figure 5(a).
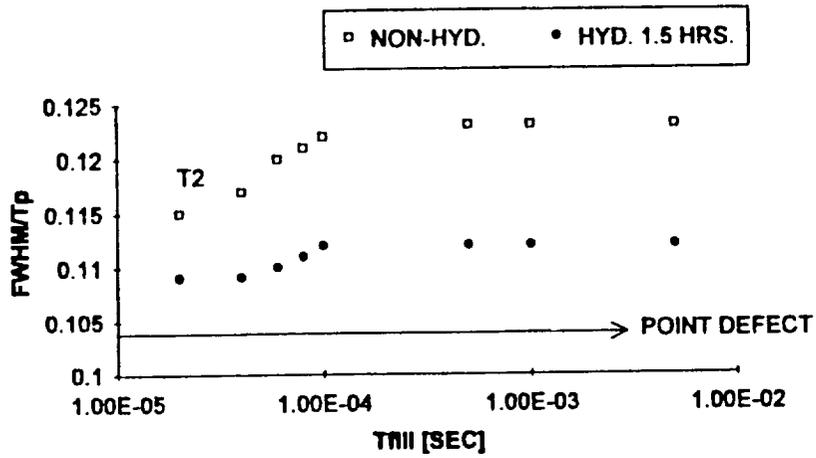
Figure 6. FWHM/T_p data for T2, as a function of fill pulse time measured before and after hydrogenation. The line at FWHM/T_p = 0.104 is calculated for an ideal point defect.
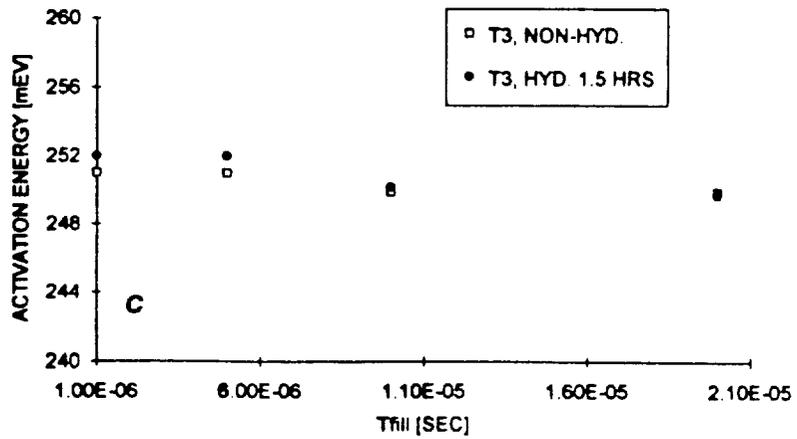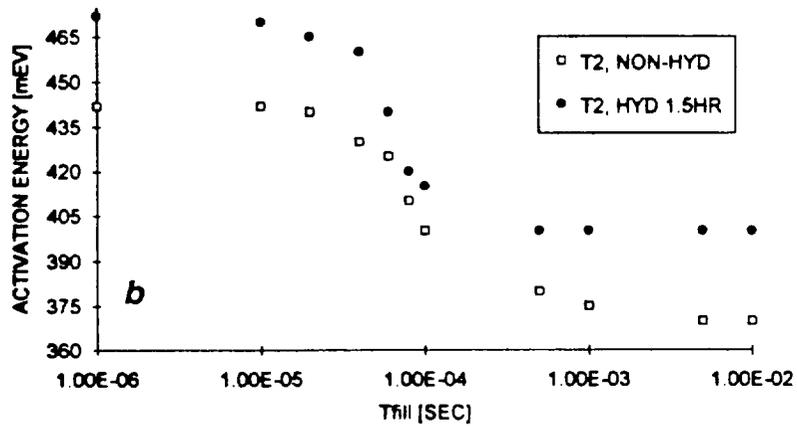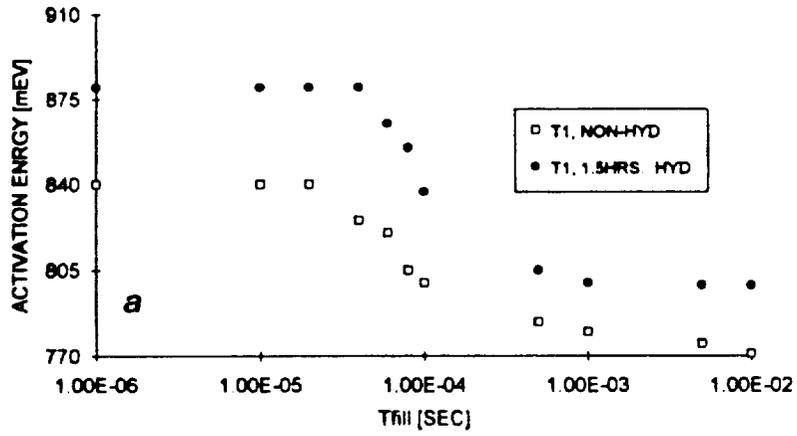
Figure 7. Variation of DLTS activation energy with fill pulse time, measured by the Arrhenius method for as-grown and hydrogenated samples for (a) T1, (b) T2, and (c) T3.