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ABSTRACT

The effect of hydrogenation on a variety of electrically active defects in bulk single crystal n-type GaAs and GaP has been observed using transient capacitance spectroscopy. Approximately half of the different defect states in these materials were neutralized by hydrogen incorporation. The efficiency of neutralization was slightly more pronounced for defects in GaAs compared to those in GaP.

The use of atomic hydrogen to bond to and to passivate electrically active defects in semiconductors is of technological and scientific interest. A great deal of experimental information has been accumulated on the types of defects that can be neutralized in Si [1-3] and Ge [4, 5], and the depth to which this can be achieved as a function of the hydrogen plasma exposure conditions. Much less is known about the passivation of defects in compound semiconductors, in which defect and impurity densities are usually higher compared to the elemental semiconductors. In this letter we report on the effects of hydrogenation of a variety of defect levels in bulk single crystal GaAs and GaP in an attempt to determine the applicability of this technique to these materials.

The samples used were cut from crystals grown at the Hewlett Packard Optoelectronic Div.'s Laboratory, Palo Alto. The n-type GaAs crystals, grown using the low pressure LEC technique, were intentionally doped with Tellurium [$(N_d-N_a)=2\times10^{17}$ cm^{-3}] or Silicon [$(N_d-N_a)=2\text{-}50\times10^{17}$ cm^{-3}]. The crystals were grown in the <111> direction and sliced to give wafers with [~100~] surfaces. The n-type GaP crystals were also grown by the LEC method, and doped with S[N_d-N_a = $2\text{-}5\times10^{17}$ cm^{-3}]. The wafers were lapped and then polished by conventional chemical-mechanical techniques to give surfaces free from damage. Hydrogenation was carried out by inserting the samples into a 13.5 MHz, 0.5 torr hydrogen plasma contained within a quartz tube. The samples were heated by placing them on a graphite block that was heated through coupling with a 440KHz R.F. field. Diode structures for capacitance spectroscopy measurements were fabricated by alloying GaIn eutectic or Au-Ge to the back face of the samples and evaporating 200 Å

thick, 0.5-1 mm diameter gold contacts on the front faces. The deep level transient spectroscopy (DLTS) measurements were performed over the temperature range 4-320K in the usual manner [6], in a system based on a 1MHz capacitance bridge and Miller correlator [7].

Figure 1(a) shows the transient capacitance spectrum of a Si doped GaAs sample. The five peaks represent electron traps with the most prominent, E(0.17) and E(0.72), present at a concentration of 4×10^{15} cm^{-3}. The peak representing the EL2 electron trap occurs at 380K for the conditions employed here. It is already known that this defect can be neutralized by hydrogen [8], and we are interested in the effects of hydrogen on some of the other levels in LEC grown GaAs. In some cases we extended our measurements to 380K, and observed EL2 present at a concentration of $\sim 10^{16}$ cm^{-3}. No shallow donor levels were observed that could be associated with EL2. We did not take into account a possible temperature dependent capture cross section in determining the energy levels of the defects, in which case the energy level may be overestimated by the activation energy for capture. We also noted a reduction in the temperature at which the DLTS peaks occurred for E(0.16), E(0.24), E(0.17) and E(0.36) as the electric field strength was increased within the diode structures, indicating that these are donor type defects. This lowering of the Coulombic barrier to emission of a trapped electron (Poole-Frenkel effect) would be absent in the case of acceptor type defects [9].

Heating a sample containing these defects for 3h at 250°C in molecular hydrogen, or a He plasma had no significant effect on the defect spectrum. Use of a He plasma is necessary to simulate the effects of plasma exposure

(ion bombardment and illumination of the samples) without having a source of H present. That is, we separate the components of the plasma. Heating for 3h at 250°C in a H plasma produced significant neutralization of the E(0.16), E(0.24) and E(0.36) defect states, as shown in figure 1(b). Measurement depth was limited by breakdown to ~0.2μm. For these plasma exposure conditions the incorporation depth of the hydrogen is expected to be ~7μm [10]. The E(0.17) and E(0.72) levels were unaffected by the hydrogenation treatment. Plasma etching of the GaAs surface did not lead to pitting and the Schottky diodes exhibited low reverse leakage currents. The Te doped GaAs displayed the same defect levels, with the exception that there was no E(0.17) state. As before the hydrogenation treatment did not affect the E(0.72) level. Hydrogenation of EL2 was confirmed by elevated temperature C-V and DLTS measurements.

In the S-doped GaP four different electron traps were observed, as shown in figure 2(a). Exposure to the hydrogen plasma neutralized two of these defect levels, E(0.50) and E(0.44), as shown in figure 2(a), again to our diode breakdown limited measurement depth (~0.2μm). The use of GaP with a much lower net impurity content is required to enable measurement of the hydrogen passivation depth attainable in this material by allowing profiling of the defect concentrations to greater depths. To our knowledge this is the first demonstration of the hydrogen passivation of deep defect states in GaP. Comparison of figures 1 and 2 showing spectra from GaAs and GaP diodes of similar net impurity content, indicates that hydrogenation at 250°C is slightly more efficient for states in GaAs as compared to GaP.

The microscopic nature of most of the defects which have been observed in compound semiconductors is yet unknown. Indeed even the structure of the dominant deep level in undoped LEC GaAs, the so-called EL2 level, is the subject of controversy [11]. The object of this paper is not to speculate on the chemical or structural nature of the deep defects measured, but rather to observe the effects of atomic hydrogen on their electrical activity. A mistaken impression could be gained from the burgeoning literature on this subject, that is, that H neutralizes all electrically active defects. However, we show here that this is not the case, and that hydrogenation will necessarily be useful only in certain instances. Indeed the fact that a defect is neutralized by hydrogen is not proof that the defect structure includes a dangling bond, as there is some evidence that hydrogen may force a solid-state reaction with some defects, and not simply satisfy a defective bond [2].

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FIGURE CAPTIONS

Figure 1. DLTS spectra recorded under the same conditions (reverse bias V_R=5V, emission rate e=100S^{-1}) for Si doped GaAs (a) as grown, and (b) after exposure to a H plasma for 3h at 250 ℃, showing neutralization of three of the defect states.

Figure 2. DLTS spectra recorded under the same conditions (reverse bias V_R=5V, emission rate e=100S^{-1}) for S-doped GaP (a) as grown, and (b) after exposure to the H plasma for 3h at 250°C..

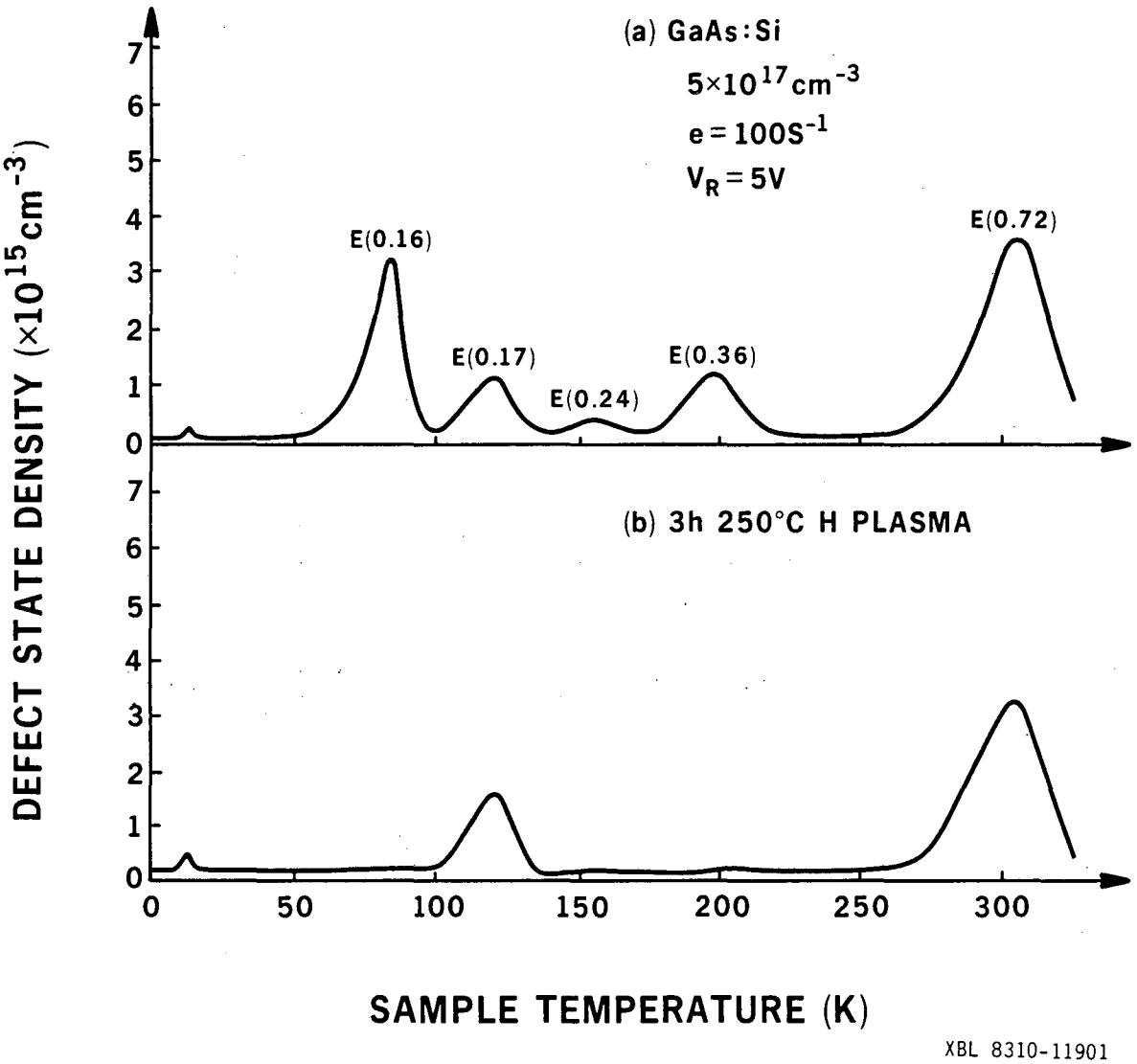
(a) GaAs:Si
5×10^17cm^-3
e = 100S^-1
V_R = 5V
E(0.16)
E(0.17)
E(0.24)
E(0.36)
E(0.72)
(b) 3h 250°C H PLASMA
DEFECT STATE DENSITY (×10^15cm^-3)
SAMPLE TEMPERATURE (K)
0
50
100
150
200
250
300
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Figure 1.

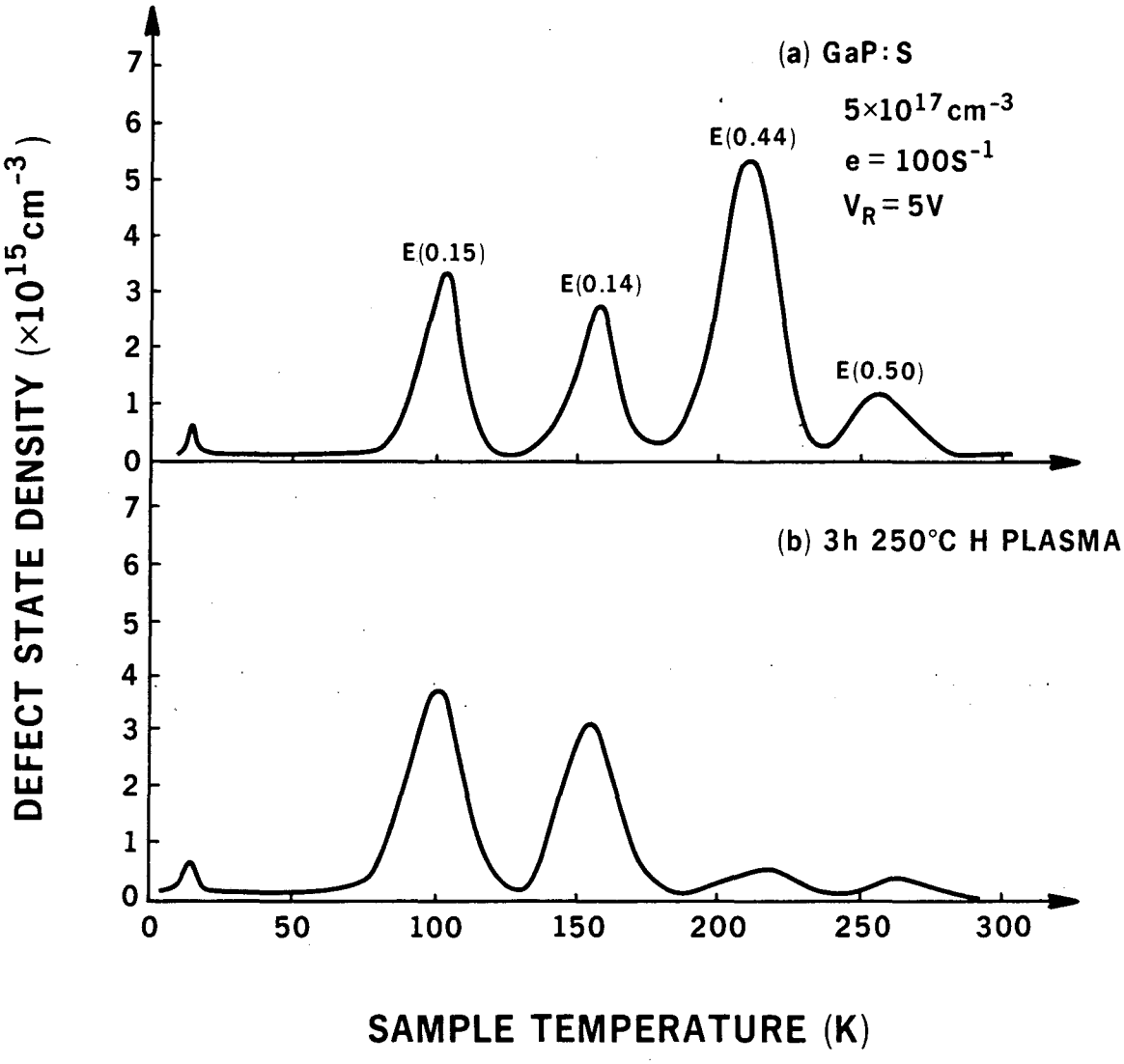

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Figure 2.

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