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HYDROGENATION OF DEEP-LEVEL HOLE-TRAPPING CENTRES ASSOCIATED WITH GRAIN BOUNDARIES IN GERMANIUM

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ABSTRACT

Effects of the hydrogenation of deep level, hole-trapping centres associated with grain boundaries incorporated in diodes from n- and p-type germanium have been examined by deep level transient capacitance spectroscopy and measurement of reverse bias leakage current. Significant reductions in diode leakage current (by factors of 2 to 10 at 77 K) and suppression of deep level centres were observed following exposure to a low pressure (0.5 torr), radiofrequency-induced hydrogen plasma at 300°C for 2 hours; no reversal was observed after a subsequent vacuum anneal at the same temperature and time.

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CRYSTAL DEFECTS; GERMANIUM; GERMANIUM DIODES; GRAIN BOUNDARIES; HYDROGENATION; LEAKAGE CURRENT; PLASMA; SPECTROSCOPY

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1. INTRODUCTION

Recently, considerable interest has been shown in the passivation by hydrogen of electrically active defects (dangling bonds) associated with grain boundaries in polycrystalline silicon [Seager and Ginley 1979a, 1979b, 1981; Campbell et al. 1979; Campbell 1980; Makino and Nakamura 1979; Makino et al. 1980] and the passifying action of other elements such as lithium [Miller and Orr 1980; Young et al. 1981], fluorine and oxygen [Ginley 1981] has also been investigated. Those studies were prompted by potential improvements in device performance, especially for use in photovoltaic cells [Seager and Ginley 1979a, 1979b, 1981; Miller and Orr 1980; Young et al. 1981] and varistors [Ginley 1981]. Results from a study of the suppression of electrical activity of grain boundaries in GaAs have also been reported by the present authors [Pearton and Tavendale 1983a].

In the case of germanium, there appears to be no published work of a similar nature, possibly because of the lesser technological importance of this semiconductor. However, apart from the consideration of materials studies which are of basic interest, passivation of extended defects in germanium by hydrogenation, if successful, could be applied to some aspects of nuclear radiation detector fabrication, photoconducting detectors, or perhaps used as a suppressor of dark currents in photo-avalanche diodes now being developed for optical fibre transmission detection [Kagawa et al. 1981]. Work at the Lucas Heights Research Laboratories has shown that point defects generated in melt-regrowth layers on germanium, produced by Q-switched ruby laser illumination, are passivated by hydrogenation [Pearton and Tavendale 1983b] and that the rate of formation of some electrically active γ-radiation defects is also retarded by pre-hydrogenation [Pearton and Tavendale 1982].

This report describes significant reductions in reverse bias leakage currents at 77 K from germanium diodes containing grain structure to varying degrees after the material was subjected to plasma hydrogenation. The suppression of carrier-trapping centres associated with these extended defects, measured by deep level transient capacitance spectroscopy, is also demonstrated.

2. EXPERIMENTAL DETAILS

Diodes were prepared from three Czochralski crystals and one zone-refined ingot grown in these laboratories. The material contained either crystallites (grains), isolated low-angle grain boundaries (lineage), or a uniform density of dislocations. The growth conditions, together with material electrical properties, are outlined in table 1; typical grain and lineage structures studied are shown in figure 1. These defect structures were exposed by etching in a hot (∿ 70°C) mixture of $4HNO_3$ (70 wt %) : 1HF (37 wt %) for five minutes. All diodes were given n^+ contacts by vapour diffusing antimony in a hydrogen ambient for one hour at 600°C in an inductively heated furnace under conditions of minimal contamination by copper (samples were pre-rinsed in strong KCN solution and mounted on similarly treated germanium substrates). For the p-type base material, the Sb-diffused layer (∿ 1 μm thick) served as the blocking contact of an n^+-p junction with a Ga-In liquid alloy film rubbed on to the rear face as an ohmic contact. Vacuum-evaporated palladium surface barrier contacts were made to the n-type base material for which the Sb-diffused layer served as an ohmic contact. Twenty diodes, including five without grain boundaries (blank samples from the two p-type crystals), were fabricated and examined; final dimensions were typically 4 mm x 4 mm x 1 mm thick.

In all cases, hydrogenation was carried out at 300°C for two hours. Samples were mounted on a resistively heated plate and exposed to a radiofrequency (27 MHz) induced plasma (∿ 0.5 W cm^{-3}) of palladium-diffused hydrogen flowing at a pressure of 0.5 torr in a silica tube. Samples were cooled while still subjected to the plasma to avoid the possible loss of hydrogen from the germanium by out-diffusion.

Gas flow was maintained by a turbomolecular pump, which was also used for vacuum annealing, i.e. for dehydrogenation under vacuum. Exposure to molecular hydrogen was made under identical conditions but without radiofrequency power. For palladium-contacted diodes, the metal deposit was removed before successive hydrogen or vacuum treatments and renewed before electrical measurement; the Sb-diffused n^+-contacts on the p-type base diodes were retained.

Effects of hydrogenation on grain boundaries were examined by measurement of diode reverse bias leakage current at 77 K and by deep level transient (DLT) capacitance spectroscopy [Lang 1974], using an exponential correlator

[Miller et al. 1975] and a 1 MHz Boonton model 71A capacitance bridge. Measurement of DLT spectra was limited to a minimum temperature of 77 K. A GaAs pulsed-light emitting diode was used to illuminate the Ge diodes when minority carrier traps were studied.

3. RESULTS

Results are given for seven diodes representative of the twenty devices examined in this study; DLT spectra were chosen on the basis of best signal-to-noise ratio and only the more detailed recorded leakage current versus reverse bias characteristics are given.

All samples containing grain boundaries showed a reduction in leakage current after plasma hydrogenation; leakage currents then increased after a subsequent vacuum heat treatment (300°C for two hours at $\sim 10^{-5}$ μm Hg) but remained significantly lower than the value before plasma hydrogenation. There was no change in current for samples heated only under molecular hydrogen or for the blank samples (no lineage or grain boundaries) heated under either plasma or molecular hydrogen. Figure 2 shows the effects of such treatments on the leakage currents of diodes from each class of material. From figures 2(a) and 2(d) it is seen that the leakage current for untreated diodes containing either lineage or grain boundaries is much higher than that for defect-free diodes from the same base material. For example, with reference to the results of figure 2(d) take the comparative photomicrographs of grain structure in diodes Ge-D-2 and Ge-D-4; the first device shows a high degree of polycrystallinity and, on hydrogenation, its leakage current is reduced; the second diode shows only a uniform dislocation density and hydrogenation does not affect the leakage current. The absence of change in leakage current after plasma hydrogenation of samples without grain boundaries also confirms that the effects observed are neither surface nor bulk in origin but are indeed associated with boundary structures. Generally, current levels were reduced by factors of 2 to 10 when diodes containing these extended defects were hydrogenated in a plasma.

The results of measurement of diode (surface barrier) DLT spectra from the highly polycrystalline n-type material (figure 3) show that no deep level majority carrier (electron) trapping centres were present, either in the as-grown, hydrogenated or vacuum heated material. However, under pulsed-light illumination, used to inject minority carriers (holes), a series of close-spaced peaks due to minority carrier trapping levels is apparent in the as-grown (untreated) material or in material heated under molecular hydrogen. The minority traps and continuum, unchanged by heating under molecular hydrogen, disappear after plasma hydrogenation and do not re-appear on further heating in vacuo, as can be seen in figure 3. Figure 4 shows the effect of plasma hydrogenation on DLT spectra taken from another diode on n-base material with lineage and containing an extended grain boundary (see diode Ge-B-2 of figure 1), again illustrating the suppression of electrically active centres associated with these structures. Only a continuum of deep level centres is apparent from this sample.

In the DLT spectra of figure 5, from a diode (Ge-A-1) made from more lightly lineaged p-type material (see figure 1), a feature observed at ∿ 77 K could be due to a single majority carrier trap; no minority (electron) traps are seen. Hydrogenation eliminates this trapping centre and it is not restored by heating in vacuo, indicating a tight bonding between the hydrogen and the defects, at least at an anneal temperature of 300°C. It is emphasised that no changes were observed in the DLT spectra from diodes heated only under molecular hydrogen.

4. DISCUSSION AND CONCLUSIONS

It appears that plasma hydrogenation of grain boundary and lineage structures leads to reductions in leakage-currents generated by deep level, electrically active centres located at these extended defects in germanium. This is almost certainly a result of the passivation or neutralisation by atomic hydrogen of dangling bonds associated with the dislocations in these structural defects, and is analogous to the behaviour of hydrogen in polycrystalline silicon.

The DLT measurements also confirm a suppression of deep level defects on hydrogenation. The observation of a continuum-like energy spectrum of deep levels in the DLT measurements of the samples in figure 3 and especially figure 4 could be interpreted as the result of the interaction of overlapping wave functions of deep centres associated with close-spaced dislocations in lineage or grain boundaries. However, the background might equally well be due to a coalescence of individual peaks, unresolved by the DLT spectrometer. In this respect, Broniatowski and Bourgin [1982] have recently measured the transient-capacitance response of grain boundary levels associated with a single boundary in an n-type germanium bi-crystal and observed a single, majority (electron) carrier-trapping centre whereas, in the present work, we have only detected minority (hole) traps in n-type material. The nature of the deep level centres obviously depends on the type (structure) of the lineage or boundary present.

It is interesting to note that Hubbard and Haller [1979] have reported DLT measurements on dislocated, high purity (chemical impurity content approximately 10^{10} cm^{-3}) germanium in which bands of hole-trapping levels were seen to be associated with dislocations at densities $\gtrsim 10^4$ cm^{-2}. For crystals grown in hydrogen, there was a shift of these energy bands, due possibly either to modification of the number and energy of multiple acceptors or to chemical origin (for example copper) by hydrogen association [Hansen and Haller 1972; Haller, et al. 1981]. (The concentration of hydrogen in germanium crystals grown under hydrogen gas is only $\approx 2 \times 10^{15}$ atoms cm^{-3} [Hansen et al. 1982] compared to $\gtrsim 10^{19}$ cm^{-3} [E.M. Lawson and E.J. Clayton, AAEC private communication] when introduced by plasma hydrogenation.)

Further, the energy bands observed by Hubbard and Haller, although associated with dislocations, were found only in the 10-50 K temperature range with no DLT response at 77 K (or above), the lower temperature limit for the measurements reported here. Their deep level centres are therefore quite different from those seen by us at lineage and grain boundaries in germanium.

It should be noted from the results reported in this work that the leakage currents of the plasma-hydrogenated, lineaged germanium diodes were, in most cases, still high in comparison with untreated, lineage-free diodes, indicating incomplete neutralisation of deep levels. However, no attempt was made to optimise the conditions of hydrogenation with respect to exposure time, plasma pressure or substrate temperature. Thus, although the practical use of the technique towards the reduction of leakage currents or lineage trapping effects on carrier transport in diode depletion layers may well be possible, as was suggested earlier, further optimisation of conditions for even more effective suppression of deep level activity is obviously desirable.

In summary, atomic hydrogen is an effective passivating agent for deep levels at extended defect structures in germanium. For future work it would be very desirable to extend the DLT measurement reported here to much lower temperatures ($\sim$ 10 K) and over a wider range of plasma hydrogenation conditions.

5. ACKNOWLEDGEMENT

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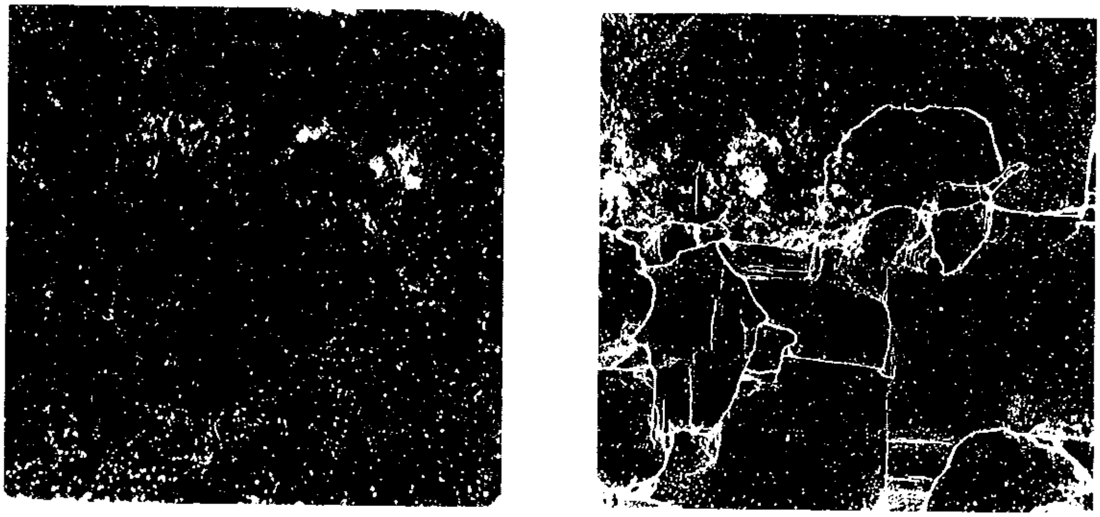
TABLE 1
GERMANIUM ELECTRICAL AND MATERIAL PROPERTIES

Diode No.	Ge Crystal or Ingot No.	Conductivity Type	Net Donor or Acceptor Concentration	Lineage/ Crystallite Boundaries
Ge-A-1	Ge-79-9-X (CZ, G)	P	$N_A \approx 1 \times 10^{15}$ cm^{-3}	Light lineage
Ge-A-2	" "	P	" "	Highly polycrystalline
Ge-A-5	" "	P	" "	Nil (single crystal)
Ge-B-2	Ge-79-8-11 (CZ, S)	n	$N_D \approx 1 \times 10^{16}$ cm^{-3}	Single extended grain boundary and lineage
Ge-C-2	Ge-NF-81-13B-11 (ZR, SZR, SM)	n	$N_D \approx 1 \times 10^{14}$ cm^{-3}	Highly polycrystalline
Ge-D-2	Ge-80-19-13-A,B (CZ, A)	P	$N_A \approx 1 \times 10^{13}$ cm^{-3}	Highly polycrystalline
Ge-D-4	" "	P	" "	Nil (single crystal)

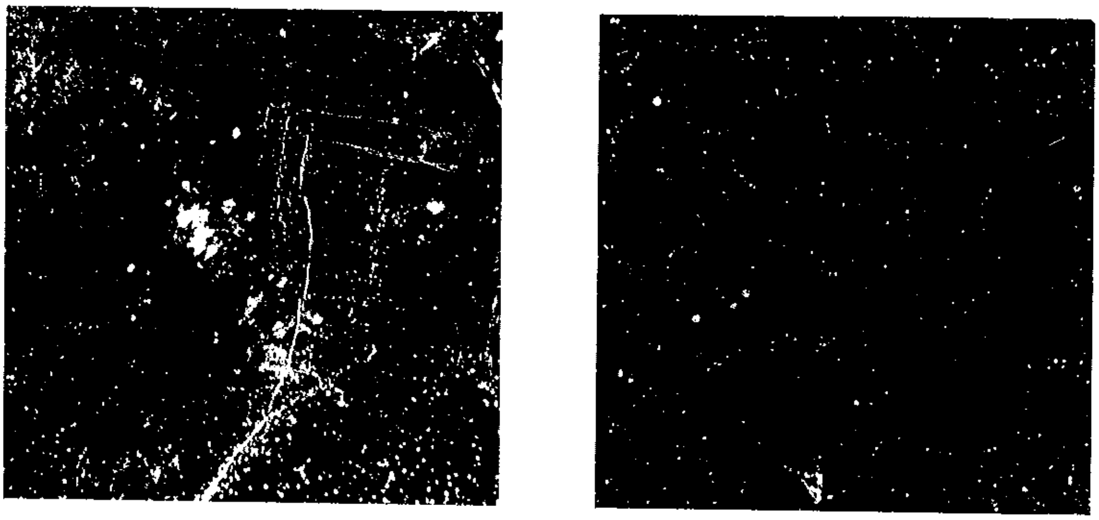
Crystal or Ingot (Bar) Preparation (see symbols in parenthesis above)

CZ	Czochralski crystal
ZR	Zone-refined ingot
S	Silica crucible
G	Graphite crucible
A	Alumina crucible
SZR	Silica zone-refiner boat
SM	Silica smoke-coated crucible or zone-refiner boat



Diode Ge-A-1

Diode Ge-D-2



Diode Ge-B-2

Diode Ge-D-4

FIGURE 1 LINEAGE AND GRAIN BOUNDARY STRUCTURES HIGHLIGHTED BY CHEMICALLY ETCHING SOME OF THE GERMANIUM DIODES USED FOR HYDROGENATION.

Diode Ge-A-1 is lightly lineaged; Ge-B-2 is more heavily lineaged with an extended grain boundary; Ge-D-2 is highly polycrystalline with a high density of grain boundaries; Ge-D-4 shows no lineage, only a uniform density of dislocations. The diodes are 4 mm on edge.

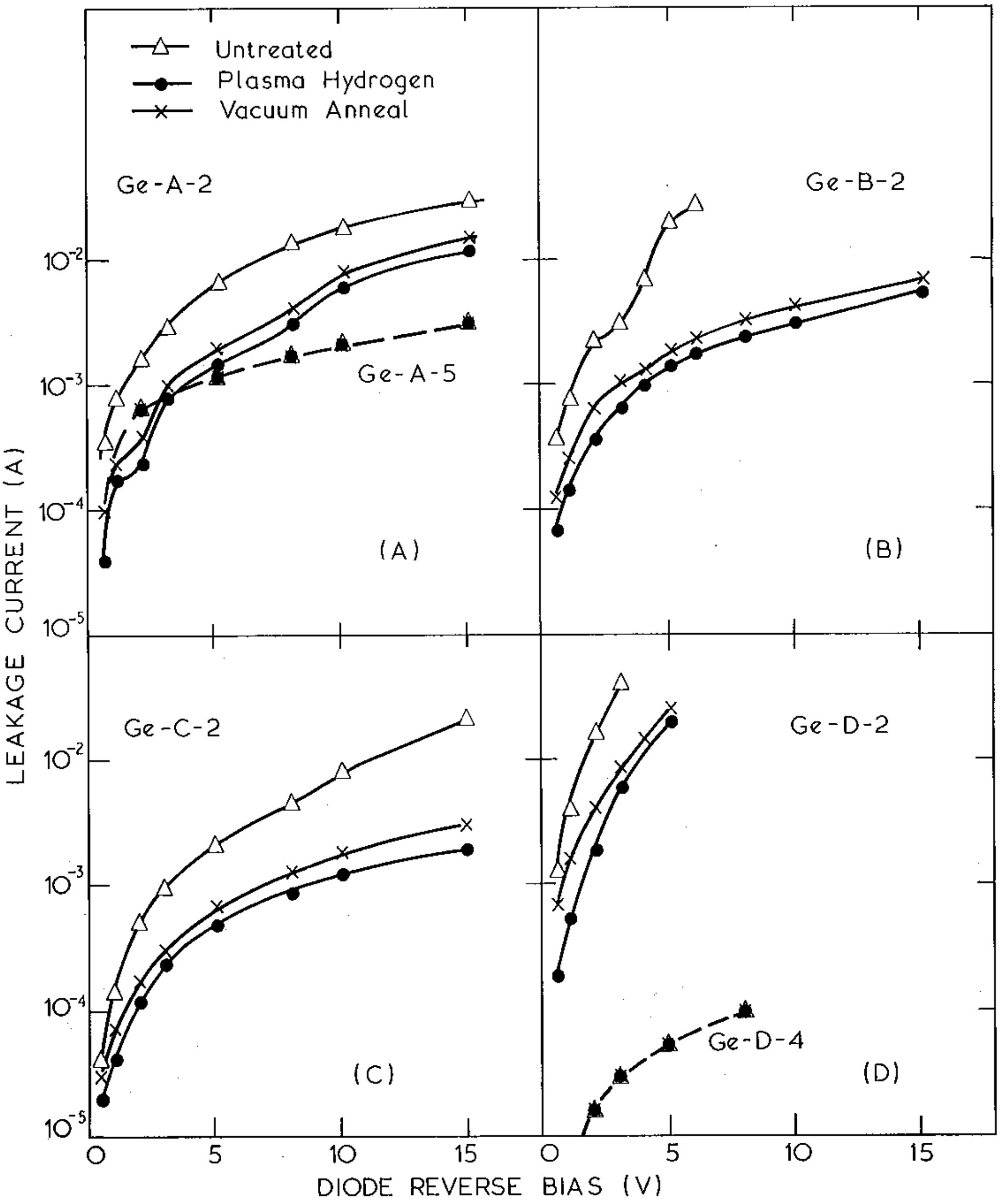


FIGURE 2 REVERSE BIAS LEAKAGE CURRENTS AT 77 K FOR GERMANIUM DIODES WITH AND WITHOUT LINEAGE OR GRAIN BOUNDARIES.

Δ, untreated; •, after plasma hydrogenation; X, after heating in vacuo following plasma hydrogenation. Diodes Ge-A-5 and Ge-D-4 (figures 2a,b) are 'blank' samples containing no lineage or boundaries and show low leakage currents.

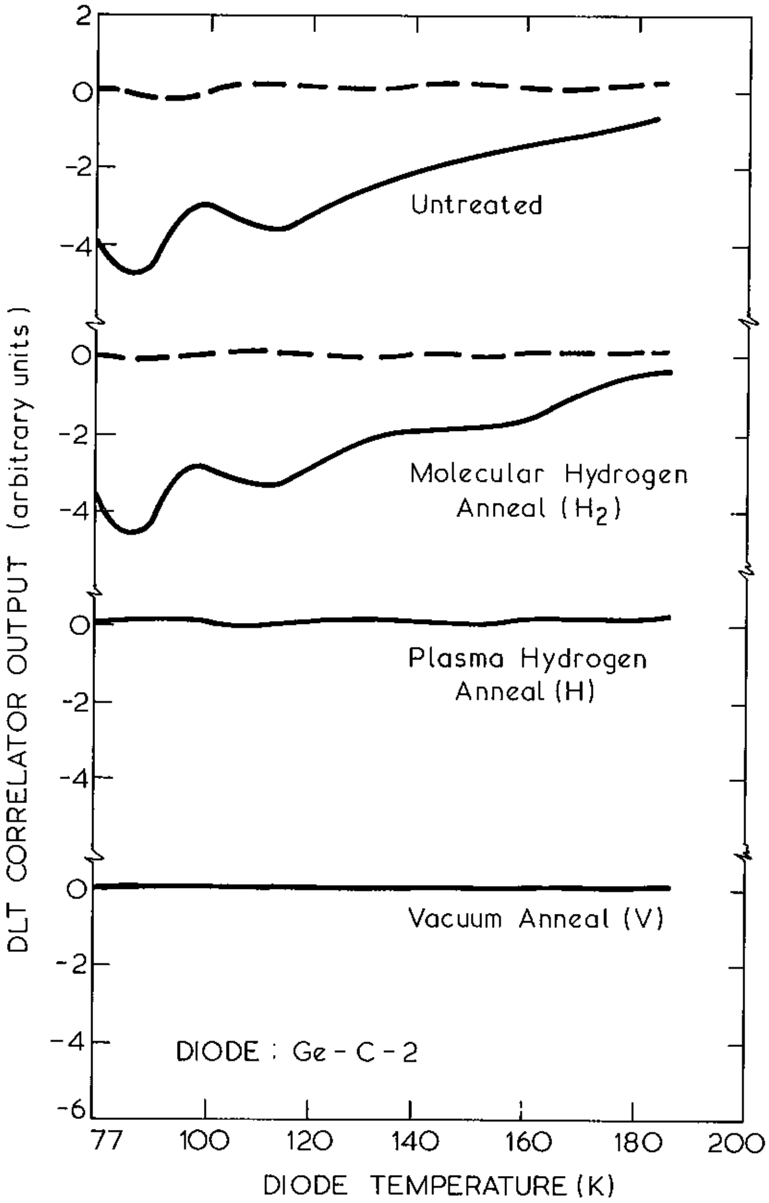


FIGURE 3 DLT SPECTRA FROM A SURFACE BARRIER DIODE ON POLYCRYSTALLINE n-TYPE GERMANIUM FOLLOWING CONSECUTIVE HEAT TREATMENTS (300°C, 2 hours) UNDER MOLECULAR HYDROGEN, PLASMA (ATOMIC) HYDROGEN THEN VACUUM ANNEAL.

The majority (electron) carrier trap response and the minority (hole) trap response are shown by the dashed and full curves respectively (reverse bias = 2 V; correlator time constant = 10 ms).

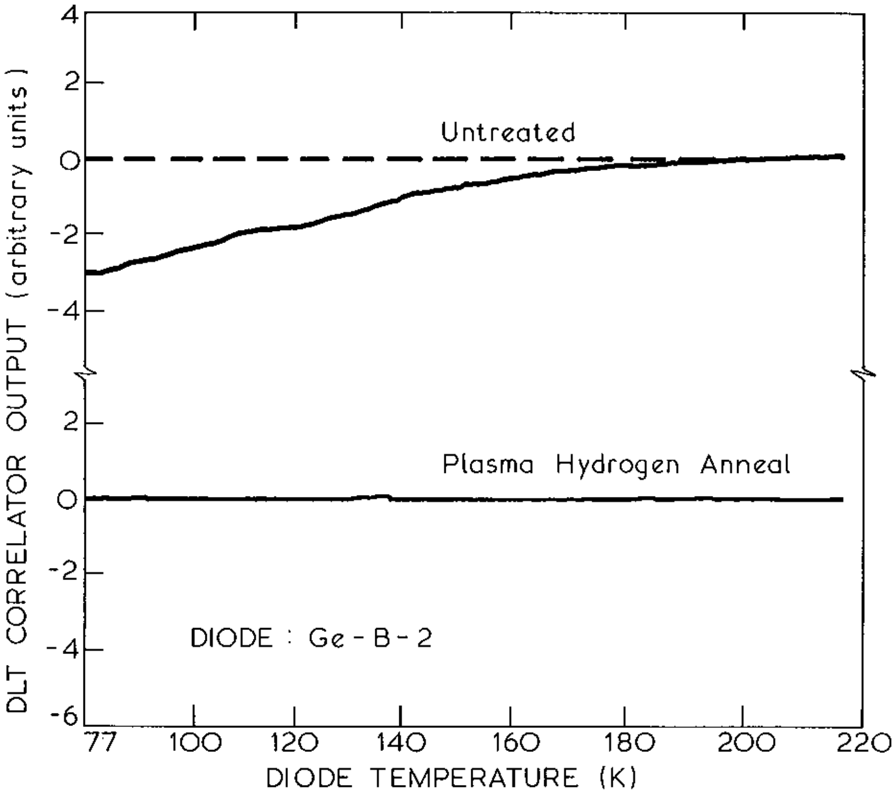


FIGURE 4 DLT SPECTRA FROM A SURFACE BARRIER DIODE ON POLYCRYSTALLINE n-TYPE GERMANIUM BEFORE AND AFTER PLASMA HYDROGEN ANNEALING (300°C, 2 hours).

DLT majority (electron) and minority (hole) carrier trap responses are shown by the dashed and full curves respectively. An energy level continuum is particularly obvious. Neutralisation of the deep level centres occurs after plasma hydrogenation (reverse bias = 2 V; correlator time constant = 10 ms).

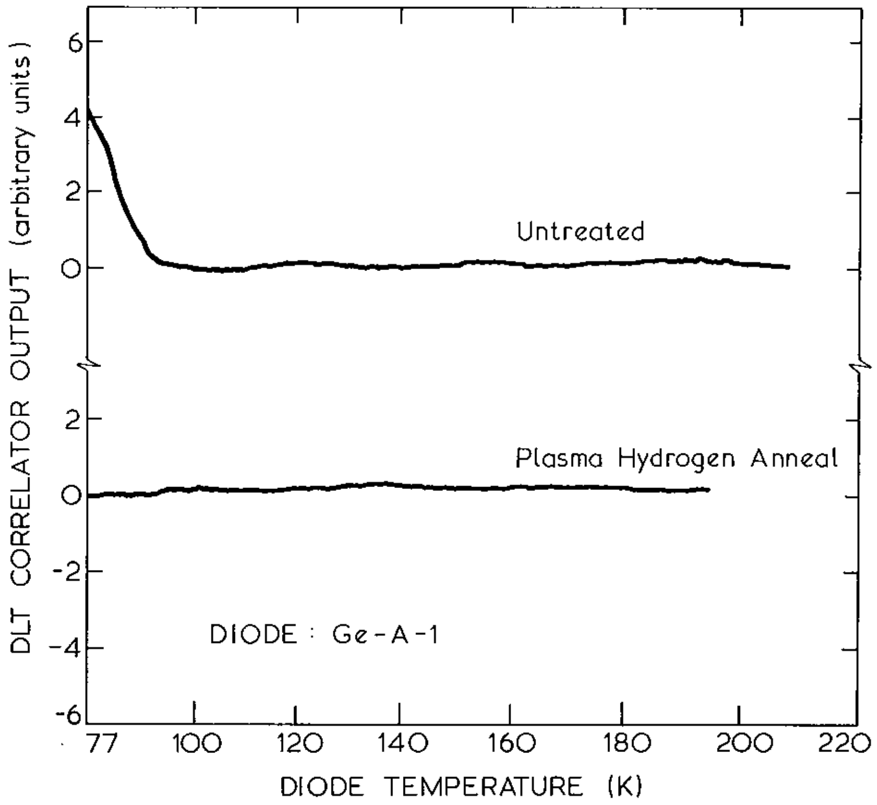


FIGURE 5 DLT SPECTRA FROM AN n^+p DIODE IN LIGHTLY LINEAGED p-TYPE GERMANIUM SHOWING MAJORITY (HOLE) CARRIER DEEP LEVEL TRAPS ONLY (NO MINORITY (ELECTRON) TRAPS WERE DETECTED) AND THE NEUTRALISING EFFECT OF A PLASMA HYDROGEN ANNEAL.
This diode does not give a continuum of energy levels as a background (reverse bias = 2 V; correlator time constant = 10 ms).