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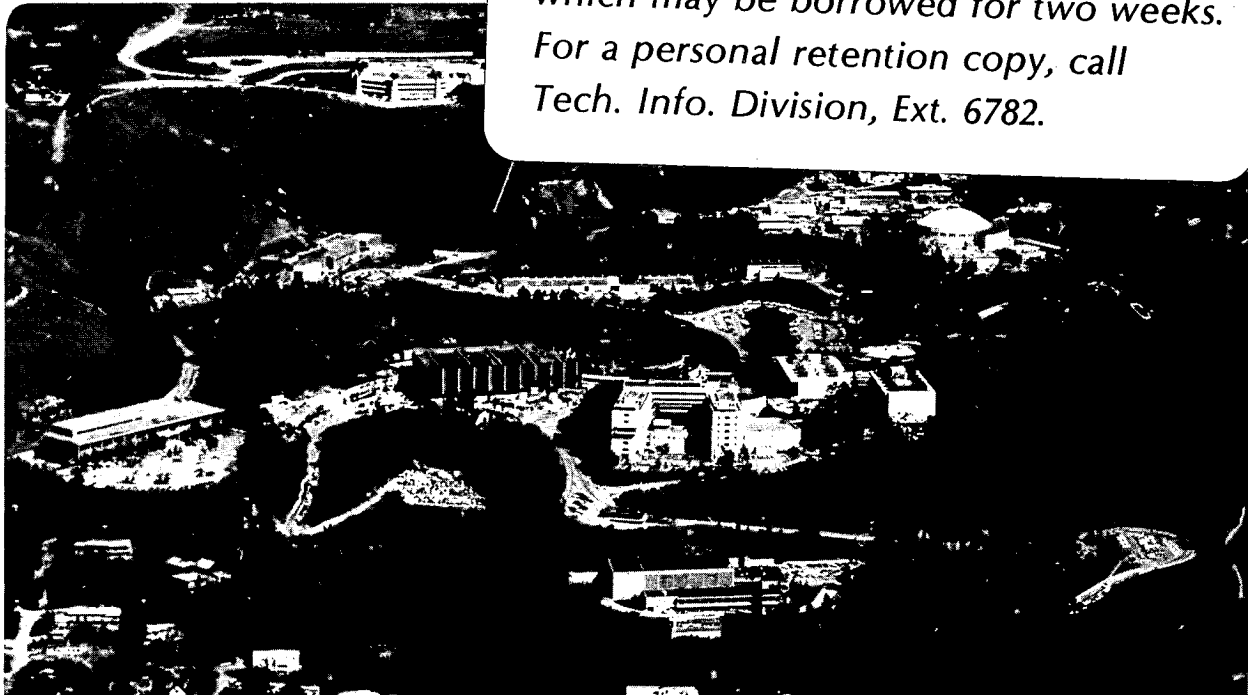
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DEEP LEVEL EFFECTS IN SILICON AND GERMANIUM AFTER PLASMA HYDROGENATION

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Abstract

Deep level electron and hole trapping states are observed in n- and p-type silicon after plasma hydrogenation at 250 - 300°C. These defect states are not observed after exposure to a helium plasma. In contrast to these results, no hydrogen or helium plasma-induced levels are seen in n- or p-type germanium after similar heat treatment of up to 600°C. However, hydrogenation of p-type germanium at 600°C significantly enhances the solubility of the rapidly diffusing impurity copper, compared to untreated material. Reproducing the experiments using a helium plasma does not affect the copper solubility. A simple model which accounts for the experimental results is proposed.

Introduction

There has been considerable recent interest in the neutralization of deep level states in silicon¹⁻⁵ and germanium^{6,7} by heating in a low pressure, radiofrequency hydrogen plasma discharge. In polycrystalline silicon, the passivation mechanism appears to be bonding of hydrogen to dangling bonds associated with grain boundaries¹⁻³. However, it is not clear if this explanation can be transferred to the neutralization of deep defect states in crystalline material. Electrical measurements, such as deep level transient spectroscopy (DLTS)⁸, indicate neutralization depths of around 10 μm in silicon and 80 μm in germanium for plasma exposures for three hours at 300°C.

Chemical identification of deuterium in silicon by secondary ion mass spectrometry (SIMS)⁹ after similar plasma treatment showed incorporation depths of less than 0.5 μm . During work to resolve this apparent contradiction, we have observed a number of interesting effects of exposing silicon and germanium samples to plasmas of hydrogen, deuterium and helium. This paper deals with the observation of deep level, electron and hole trapping states in n- and p-type silicon after hydrogenation, and notes an enhanced solubility of copper in p-type germanium after hydrogen plasma treatment. These effects are not observed after treatment for the same conditions in a helium plasma.

Experimental

The n-type silicon sample (phosphorus doped, 10^{14}cm^{-3}) and p-type silicon samples (boron doped, $10^{13} - 4 \times 10^{14}\text{cm}^{-3}$) were 2 mm thick slices cut from floating zone crystals with a zero dislocation density. The ultra-pure n-type ($N_D - N_A = 3 \times 10^{11}\text{cm}^{-3}$) and p-type ($N_A - N_D = 2 \times 10^{11}\text{cm}^{-3}$) germanium samples were also 2 mm thick slices taken from crystals grown by the Czochralski technique from quartz crucibles under an H_2 atmosphere. The dislocation density in all samples was $\sim 10^3\text{cm}^{-2}$. The germanium samples were contacted before hydrogenation by implanting 25 keV boron and phosphorus ions to opposite faces of the slices. After an annealing cycle, this produced thin, stable p^+ and n^+ contacts respectively. Contacts to the silicon samples were fabricated after the plasma exposures by evaporating gold and aluminum to opposite faces.

Samples were exposed to 0.1 Torr, 300 W, 27 MHz plasmas of hydrogen, deuterium or helium by insertion in a vacuum pumped quartz tube. Radiofrequency power from two generators was coupled to the tube via copper coils; the 27 MHz source excited the plasma, while a 550 kHz source provided power to heat the graphite block on which the samples were mounted. The heat treatments were performed at 250 - 300°C for two to three hours for both silicon and germanium samples, and at 600°C for five hours for some of the germanium slices. Heating in the molecular gases was done in the same apparatus under the same conditions, except that no plasma was present.

The DLTS measurements were performed in the usual way¹⁸ using the correlator technique¹⁰. As an additional check on the introduction of deep level states, thermally stimulated capacitance (TSCAP)^{11,12} scans at 1 MHz were also recorded. The concentration profiles of the observed deep level defects were obtained using the fixed bias, variable pulse method^{8,13}. No attempt was made to observe minority carrier traps in the samples.

Results

Figure 1(a) shows the DLTS spectrum obtained from an n-type silicon sample after hydrogenating at 250°C for two hours. The electron trapping state observed had a T^2 -corrected activation energy of $E_c - 0.53$ eV, with an electron capture cross section of $\sim 2 \times 10^{-17} \text{ cm}^{-2}$, calculated from the intercept of the Arrhenius plot (Fig. 2). The peak concentration of this center was $\sim 3 \times 10^{13} \text{ cm}^{-3}$ near the surface of the sample, and the differential pulse method showed a

diffusion-type concentration profile of the deep level (Fig. 3). It is interesting to note an unresolved DLTS feature on the low temperature side of the main peak in Fig. 1(a), which also was not observed in the control samples [Fig. 1(b)]. Samples from the same slice heated in a deuterium plasma produced the same defects as the hydrogen plasma, but heat treatment for the same conditions in either molecular hydrogen or deuterium, or a helium plasma did not induce these deep electron traps.

Samples of p-type silicon (net acceptor concentration $4 \times 10^{14} \text{cm}^{-3}$) were also given hydrogen plasma treatments at 250°C for two hours, but displayed only low concentration peaks in the capacitance transient spectra. Using samples of purer material (net acceptor concentration 10^{13}cm^{-3}) allowed these peaks to be examined more fully, as displayed in Fig. 4(a). The observed deep hole trapping state had a T^2 -corrected activation energy of $E_V + 0.45 \text{ eV}$, with a hole capture cross section of $\sim 10^{-17} \text{cm}^2$ calculated from the intercept of the Arrhenius plot (Fig. 2). The density of the level was $\sim 6 \times 10^{11} \text{cm}^{-3}$ for a two-hour, 250°C hydrogen plasma exposure, and displayed a decreasing profile evident to $8 - 10 \mu\text{m}$, similar to that of the electron trap in n-type material. Again, heating in molecular hydrogen or a helium plasma for the same conditions as for the hydrogen plasma did not produce any deep levels evident on the DLTS trace.

Samples of n- and p-type germanium were also exposed to hydrogen plasma for three hours at 300°C , but did not show any induced deep levels. Even increasing the plasma exposure to five hours at 600°C did not create any plasma related levels, although in the p-type material a low concentration ($\sim 5 \times 10^9 \text{cm}^{-3}$) of copper-related defects was evident after such a heat treatment (Fig. 5). It is difficult to exclude the rapidly diffusing copper from heat treated germanium at

temperatures much above 450°C. Again, similar results were obtained after heating in a deuterium or helium plasma, or in molecular hydrogen or deuterium.

Hydrogenating the p-type material at 600°C for five hours, however, had a significant effect on the solubility of copper subsequently introduced. Figure 6 shows the enhanced solubility of copper in prehydrogenated samples compared to unhydrogenated samples. Samples were given the five-hour, 600°C hydrogenation treatment, then heated together with samples taken from the same slice (but not exposed to any plasma) for five hours at 450°C under flowing argon gas in a furnace known to contaminate samples with copper. The increased concentration of copper in the prehydrogenated material could not be explained as a result of extra copper contamination during the plasma treatment. Another set of samples was first exposed to a helium plasma for five hours at 600°C, then heated along with control samples at 450°C in the contaminated furnace, and showed no difference in copper content. Heating initially in molecular hydrogen or deuterium before contamination by the copper also had no effect on the copper solubility. It should be noted that all the copper concentration profiles measured were constant to depths of ~ 300 μm, either at the higher concentration of the hydrogen plasma exposed samples, or the lower density of the untreated samples.

Discussion

The deep level state induced in n- and p-type silicon by hydrogen plasma treatment adds further to the mystery of the hydrogen incorporation depth in

crystalline material. DLTS measurements reveal these defect states present to a depth of $\sim 10 \mu\text{m}$, and if they are hydrogen related, then an anomalous low concentration diffusion tail of hydrogen is required to be consistent with the earlier SIMS results which show hydrogen incorporation depths of $< 0.5 \mu\text{m}$ ⁹. We have attempted to simulate other effects of plasma treatment, such as the high level of illumination and particle bombardment, by using a helium plasma, but in this case, no deep levels are induced. It may also be possible that the high concentration of hydrogen incorporated in the near surface region creates sufficient local strain in the lattice which facilitates defect generation. The effects of a possible "vacancy or interstitial wind" created in the near surface region and diffusing rapidly into the bulk may help explain the observed phenomena. It is noteworthy that quenched-in defects in p-type silicon typically lead to levels around $E_V + 0.4 \text{ eV}$ ^{14,15}. Also, Lang *et al*¹⁵ have postulated that families of deep levels exist in silicon, with the quenched-in level being the basic defect. The addition of impurities such as gold, silver or cobalt act to change only slightly the observable electrical properties, and in n-type material these impurities create "vacancy-like" electron traps at around $E_C - 0.55 \text{ eV}$ ^{15,16}. We assume the striking agreement between the hydrogen-plasma-induced levels and the quenched-in defect levels may not be coincidental but may be related to vacancies created during the plasma treatment. It is also possible that enhanced diffusion of a surface impurity could be responsible for these levels, even though no defects were observed in the helium-plasma-treated samples--the hydrogen plasma may be more efficient in aiding creation of vacancies and interstitials. Indeed at higher temperatures ($T > 750^\circ\text{C}$), we have observed severe hydrogen plasma etching of germanium samples.

The absence of plasma-induced defect states in germanium is perhaps not surprising. Hydrogen seems to bond much more strongly to silicon atoms than to germanium atoms, and preliminary SIMS results have shown hydrogen concentrations two orders of magnitude lower in the near-surface region of plasma-treated germanium, compared to plasma-treated silicon. As well, there is no consensus on the basic quenched-in, or vacancy-like levels in germanium, unlike silicon.

The observation of an enhanced copper solubility in hydrogen-plasma-treated samples is an additional result which, with further experimentation, could lead to an understanding of the puzzling trends in the solubility of this most common contaminant in germanium. It has been previously noted that the concentration of substitutional copper may vary by over two orders of magnitude in ultra-pure crystals grown under a variety of conditions¹⁷, and also that the presence of hydrogen in the crystal growth ambient seems to increase the copper concentration^{17,18}.

It is clear that highly specific and sensitive experiments are needed to unify the somewhat confusing, presently available results on the hydrogen incorporation depth and passivation mechanism in plasma hydrogenated, crystalline material. One possibility we are pursuing is the use of tritium plasmas and the self-counting nuclear radiation detector technique^{17,18} to determine the hydrogen solubility and diffusion depth in semiconductors.

Summary

Results were presented on hydrogen-plasma-induced deep levels in n- and p-type silicon. Similar exposures to a helium plasma did not produce these defects, and no levels were observed in n- and p-type germanium exposed to plasma even at much higher temperatures. Processing in a hydrogen plasma produces an enhanced solubility of subsequently introduced copper in p-type germanium, compared to control samples.

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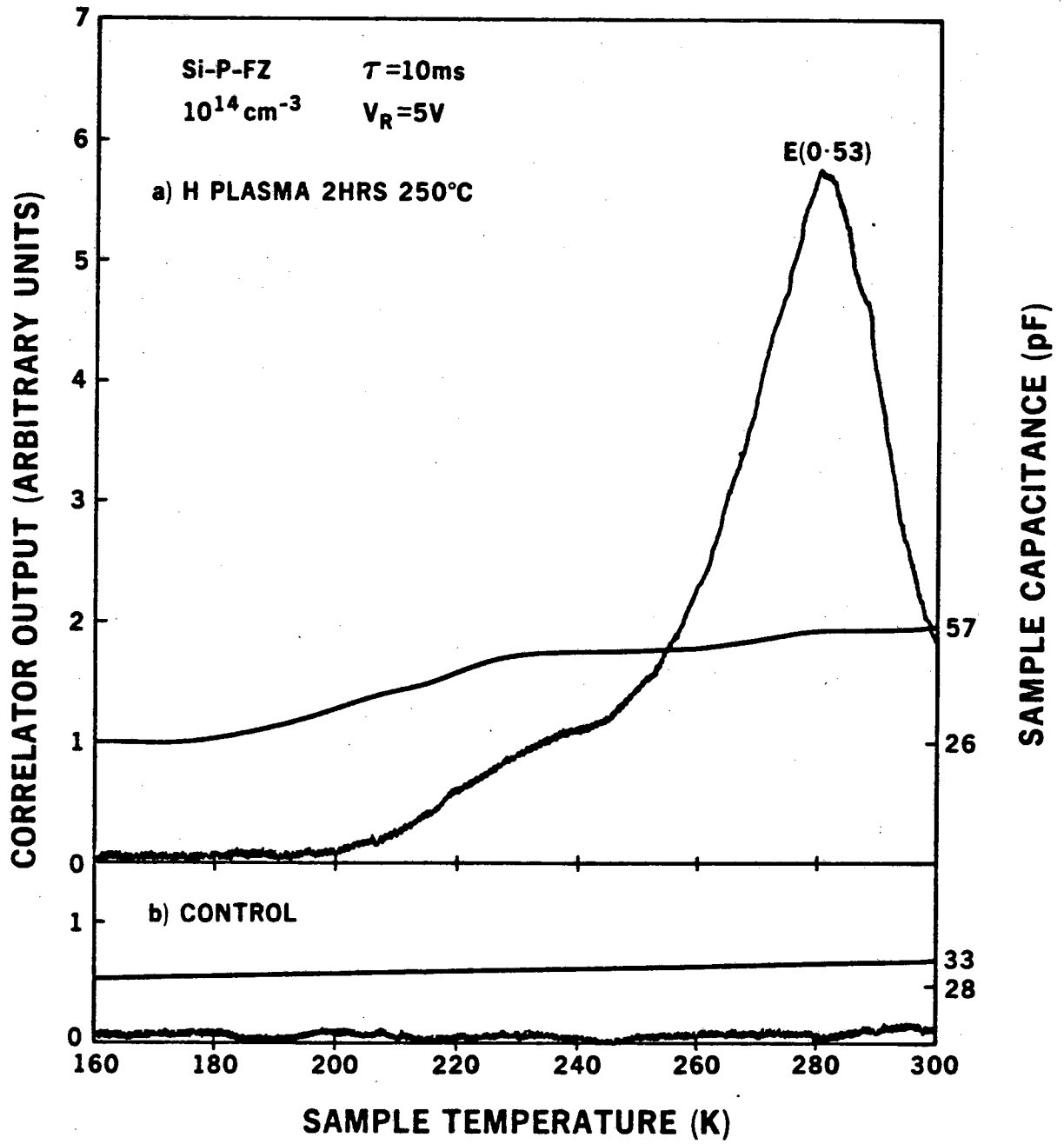
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Figure Captions

1. DLTS spectra and TSCAP scans (1 MHz) recorded under the same conditions (reverse bias $V_R = 5$ V and correlator time constant $T_C = 10$ ms) for (a) an n-type silicon sample exposed to a hydrogen plasma for two hours at 250°C , showing a deep electron trap at $E_C - 0.53$ eV; and (b) n-type silicon control sample from the same slice, showing no deep levels. Heating for two hours at 250°C in a helium plasma, or in molecular hydrogen or deuterium did not alter the DLTS trace.
2. Arrhenius plots of the two deep plasma-induced levels in n- and p-type silicon.
3. Concentration profile of the E (0.53) hydrogen plasma-induced level in n-type silicon, as determined by DLTS fixed bias, variable pulse measurements.
4. DLTS spectra and TSCAP scans (1 MHz) recorded under the same conditions ($V_R = 5$ V, $T_C = 10$ ms) for (a) p-type silicon sample exposed to a hydrogen plasma for two hours at 300°C showing a deep hole trap at $E_V + 0.45$ eV; and (b) p-type silicon control sample from the same slice showing no deep levels. Heating for two hours at 300°C in a helium plasma, or in molecular hydrogen, did not alter the DLTS trace.
5. DLTS spectra recorded at $V_R = 5$ V and $T_C = 10$ ms for (a) p-type germanium hydrogenated at 600°C for five hours. All of the peaks are copper related and the most common are labelled. There were no plasma-induced

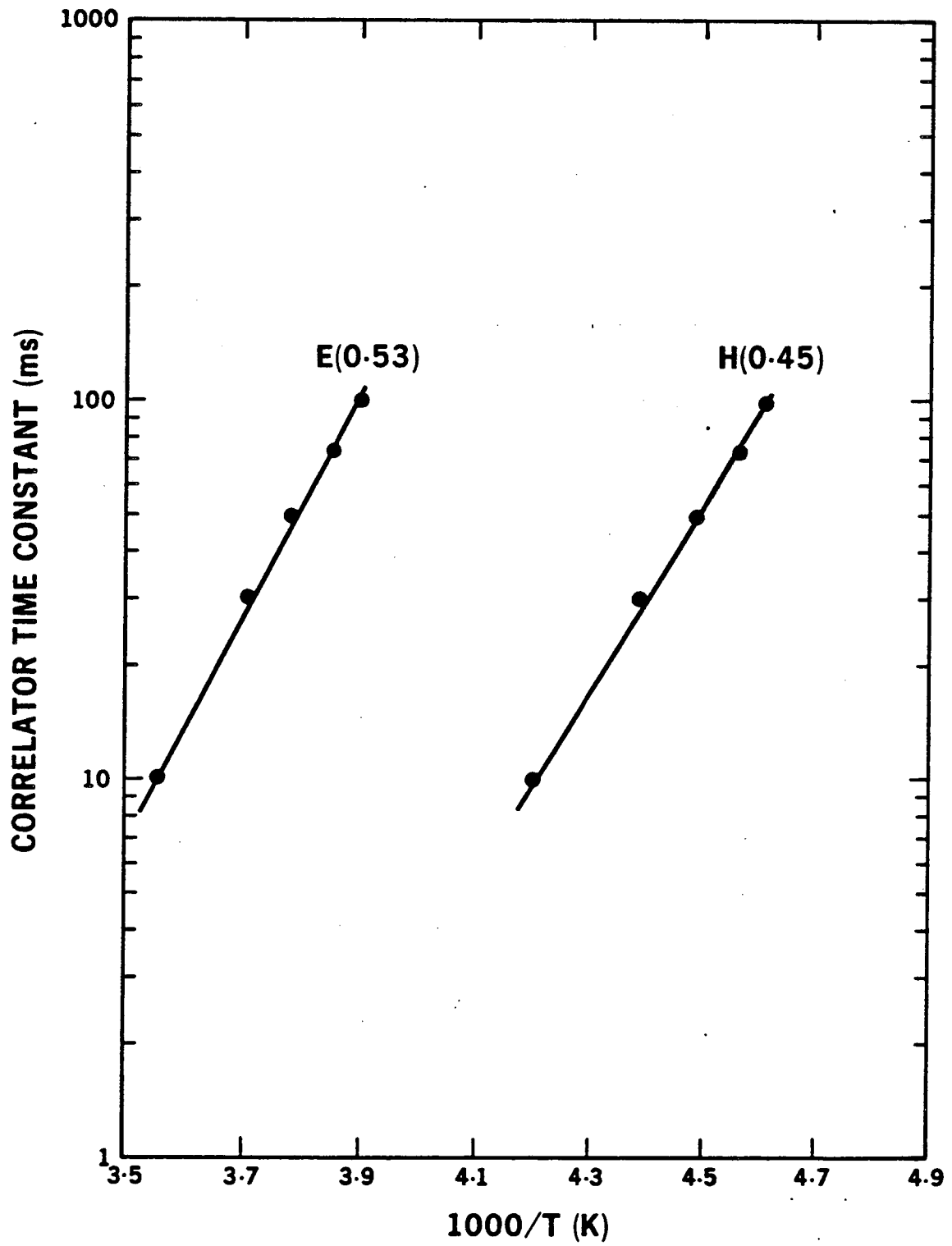
levels; (b) n-type germanium after hydrogenation for five hours at 600°C. No plasma-induced levels were evident.

6. DLTS spectra recorded at $V_R = 5$ V and $T_C = 10$ ms for p-type germanium (i) hydrogenated for five hours at 600°C (ii) heated in molecular hydrogen for five hours at 600°C. Both samples were then heated in a copper-contaminated furnace for five hours at 450°C under argon. The prehydrogenated sample shows enhanced solubility of copper. This was observed only for samples heated in a plasma of hydrogen; heating in a helium plasma, or not heating at all before the copper contamination did not significantly affect the copper solubility. Note the usual CuH levels are absent in these spectra because of the significant outdiffusion of unbound hydrogen during the heating in argon.



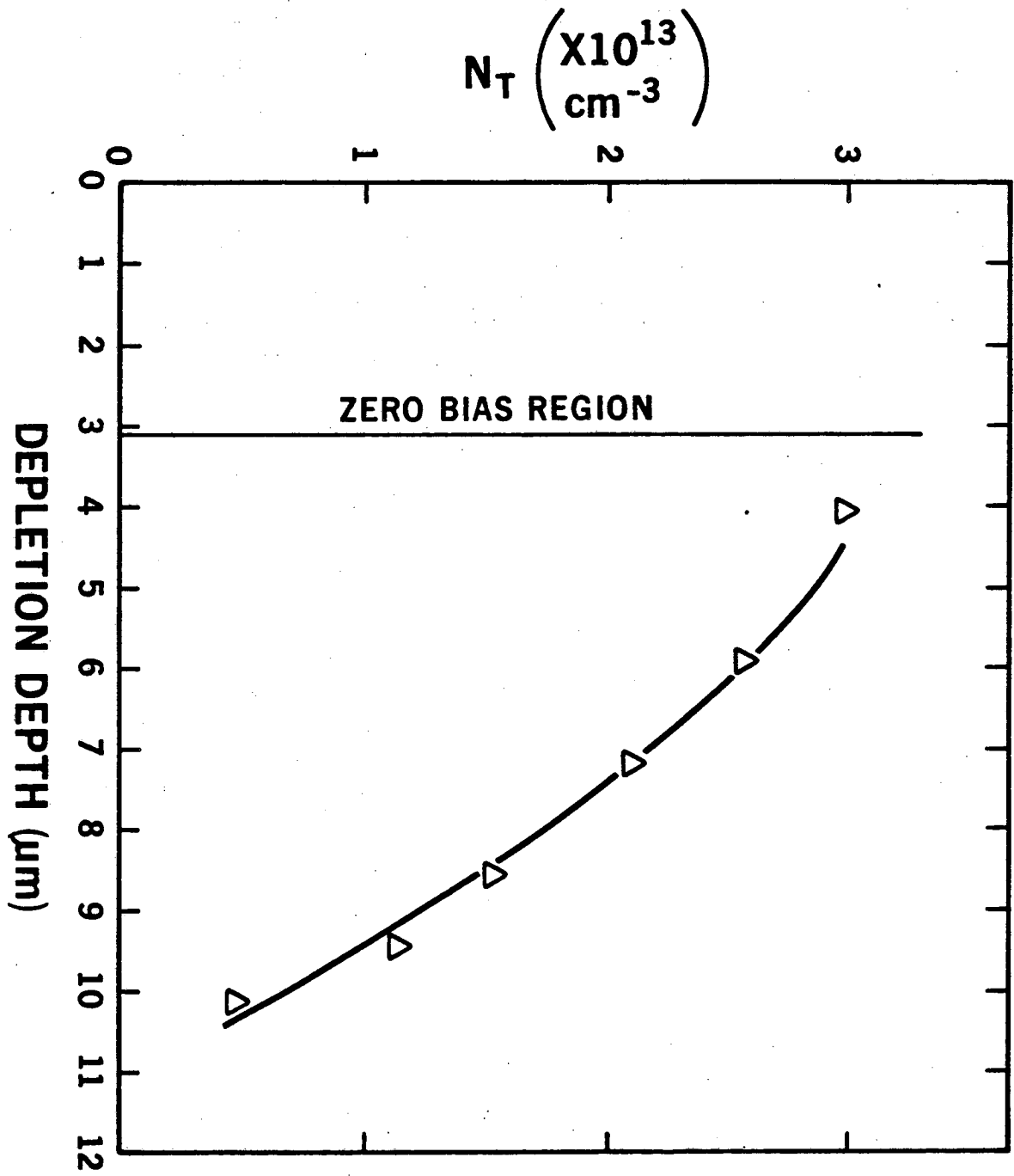
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Fig. 1



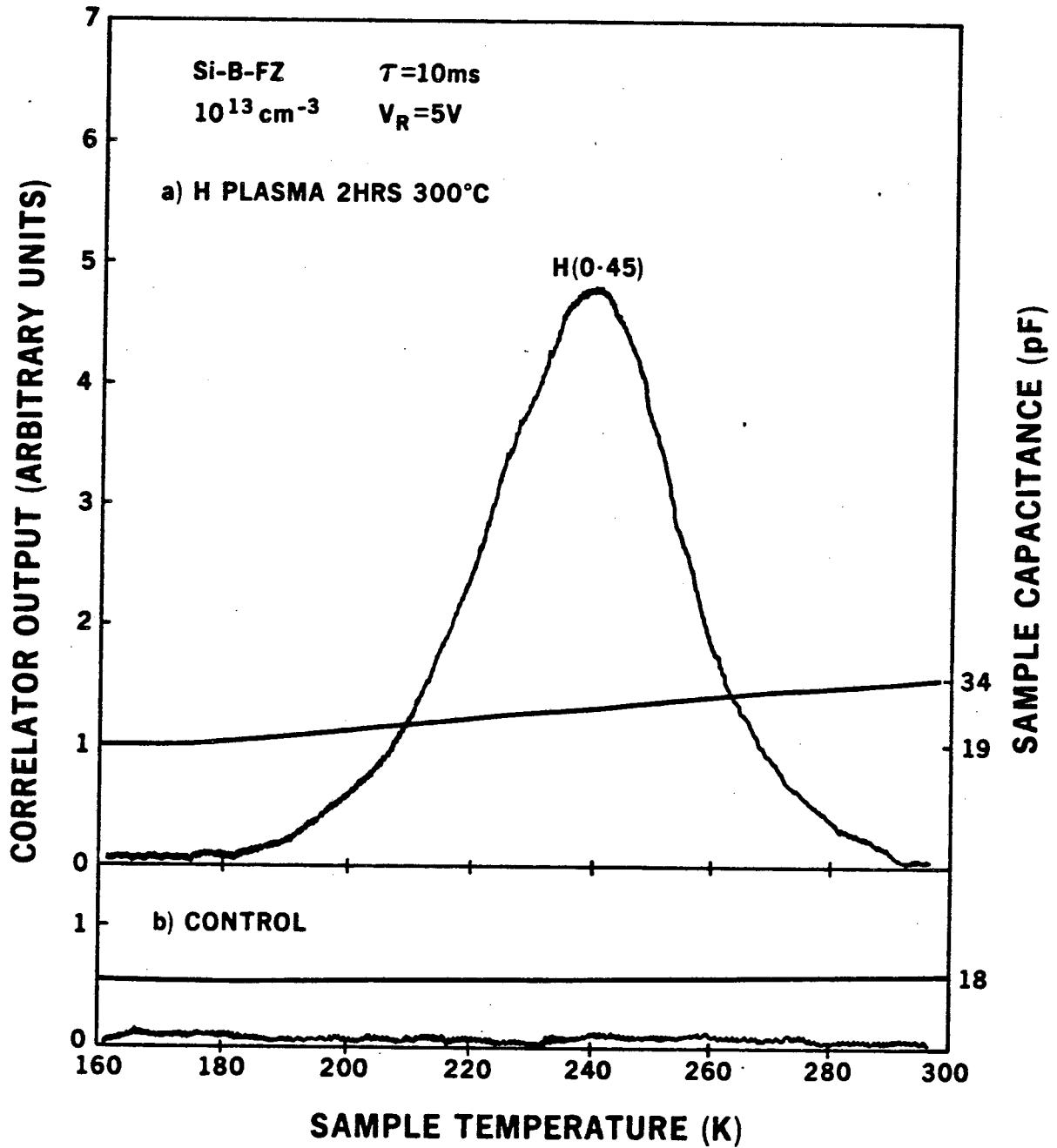
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Fig. 2



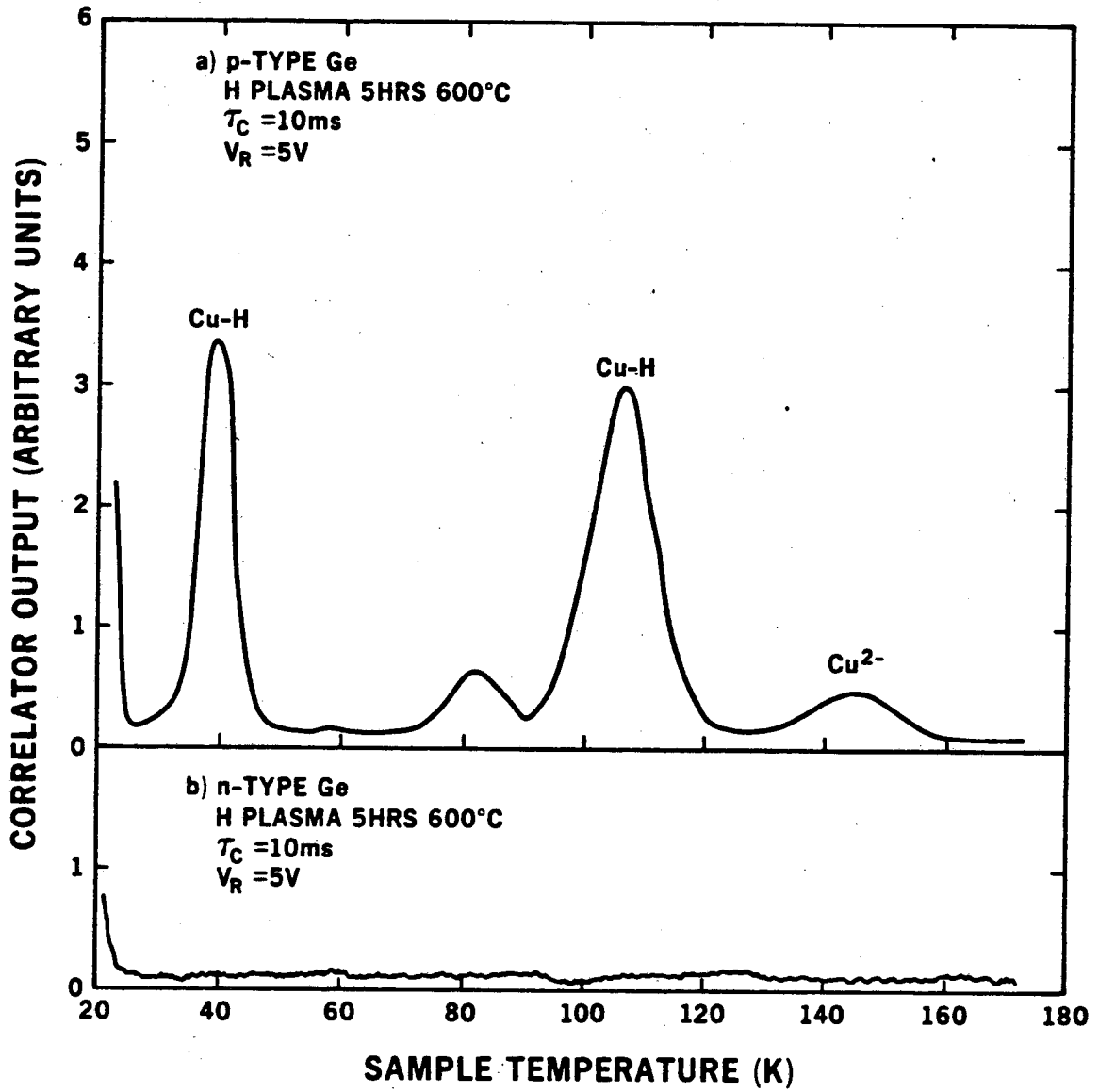
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Fig. 3



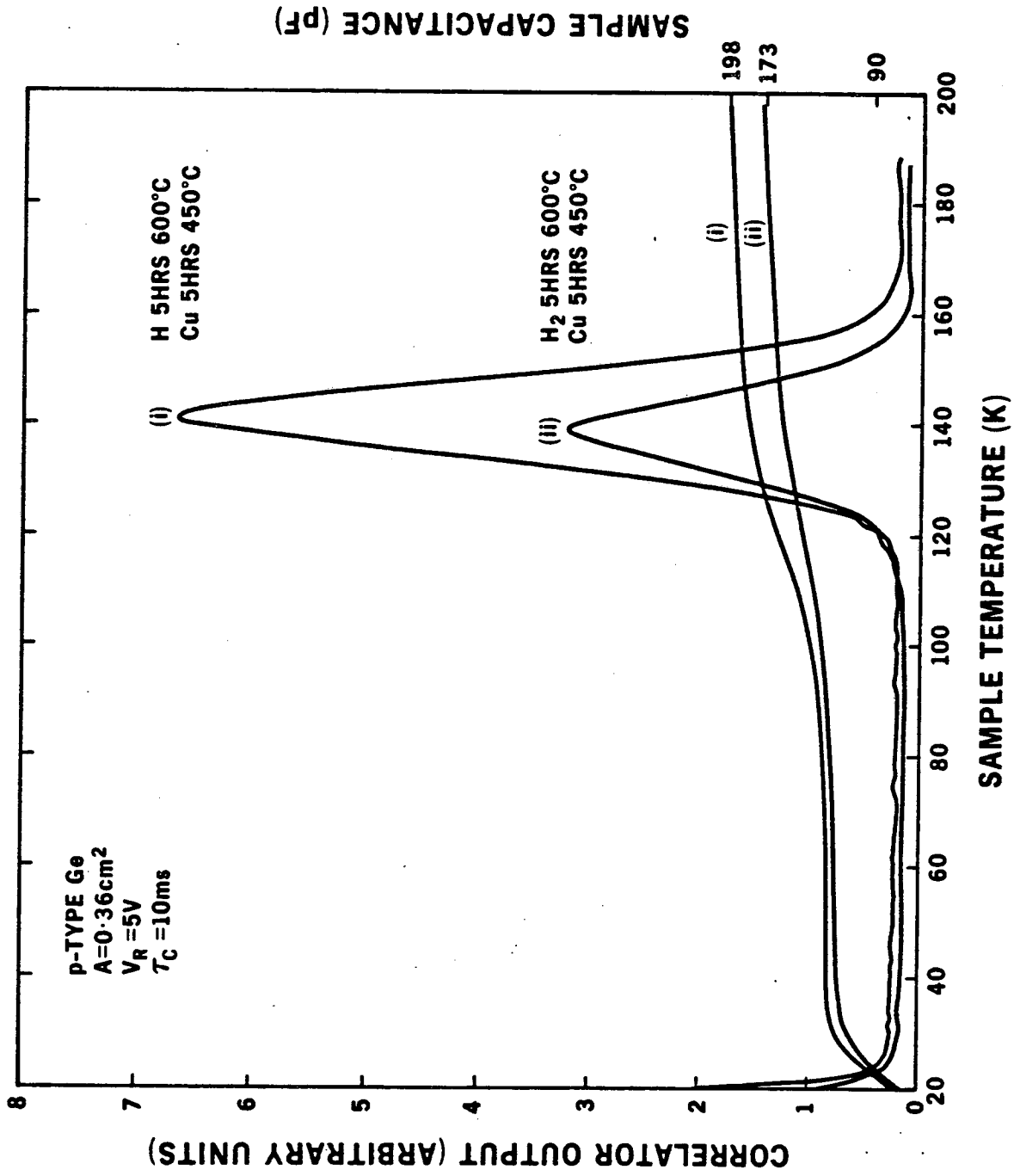
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Fig. 4



XBL 834-9072

Fig. 5



XBL 834-9074

Fig. 6

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