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April 1983

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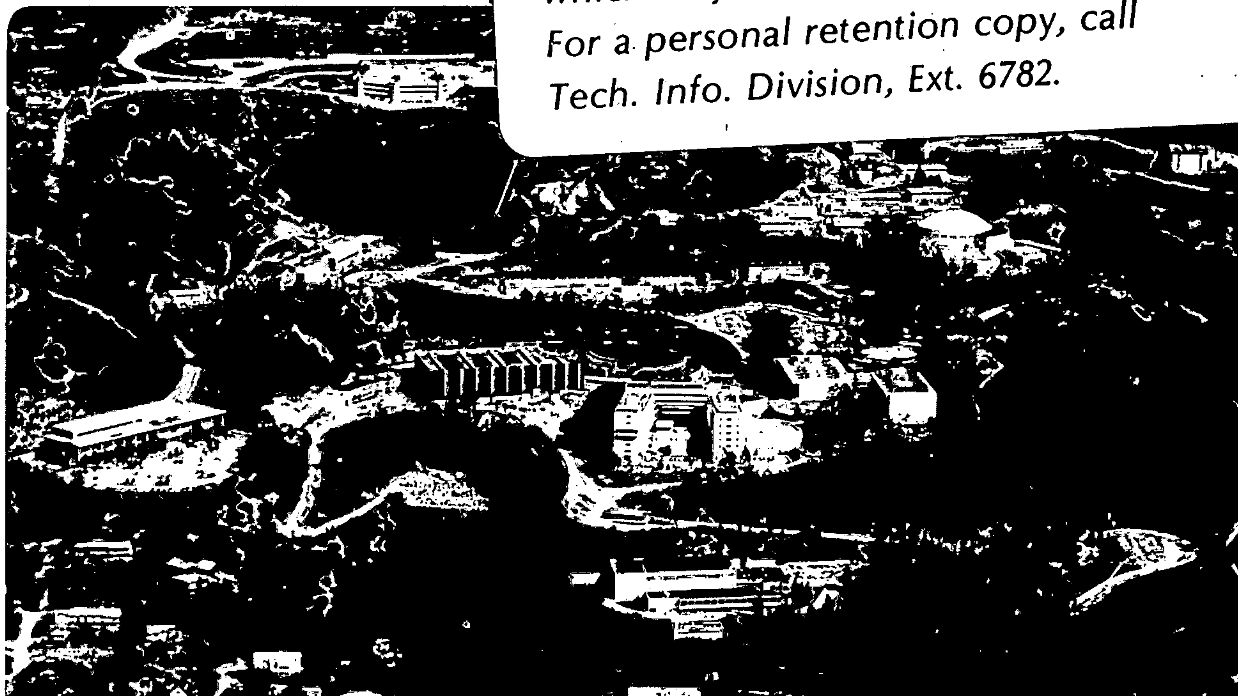

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Abstract

Electrical measurements on deuterium plasma-treated germanium samples containing deep level recombination centers show significant neutralization of these defects to depths of ~ 80 μm. Chemical measurement of the deuterium profile after similar plasma treatment shows apparent incorporation depths of ~ 0.2 μm. We discuss experiments which resolve this discrepancy, and show that hydrogen diffusion into the bulk of the germanium is responsible for the observed neutralization.

Introduction

The incorporation of atomic hydrogen into semiconductors has many beneficial effects. For example, in amorphous silicon, the room temperature resistivity can be varied by several orders of magnitude after the inclusion of atomic hydrogen[1]. High concentrations of hydrogen (up to 50% atomic) can be incorporated into amorphous material by a variety of methods, including ion-implantation, deposition from a silane plasma, sputtering in the presence of hydrogen, or evaporation followed by hydrogen plasma exposure[2-4]. In polycrystalline material, hydrogenation neutralizes the recombination properties of grain boundaries[5-7]; while in crystalline material, passivation of deep level point defects has been observed in germanium[8,9] and silicon[10-12] after heating in a hydrogen plasma. Whilst in polycrystalline semiconductors deep hydrogen incorporation depths may be achieved by preferential diffusion along grain boundaries, in single crystal material one must rely on bulk diffusion. It is in the latter case that apparent discrepancies are found between chemical and electronic measurement of the hydrogen incorporation depth.

The generally used method of observing neutralization of point defects in crystalline material is the comparison of transient junction-capacitance spectra of diode structures before and after exposure to a plasma. The deep level transient spectroscopy (DLTS)[13] method, combined with thermally stimulated capacitance (TSCAP)[14,15] scans at varying reverse bias, can give the depth profile of a recombination center. For a typical three-hour exposure to a hydrogen plasma with the sample held at 300°C, such measurements show neutralization of many different types of crystal defects to depths of ~ 80 μm in germanium, and ~ 10 μm in silicon. It is then assumed that the neutralization is due to hydrogen bonding to bonds associated with the defects, and hence

that the neutralization depth observed is simply the hydrogen penetration depth. Subsequent heating of the diode in vacuum often causes a partial reappearance of the defect states over this depth, and is ascribed to evolution of the hydrogen from the sample.

Recently, however, direct measurement of the deuterium profile in plasma treated crystalline silicon samples by Secondary Ion Mass Spectrometry (SIMS) has shown error-function profiles[6] which when extrapolated from the SIMS sensitivity ($\sim 10^{17}cm^{-3}$) to the DLTS measurements range ($\leq 10^{13}cm^{-3}$) give hydrogen incorporation depths of ~ 0.2 μm, for the same plasma conditions (Fig. 1). DLTS measurements lead to a diffusion coefficient of hydrogen in silicon at 350°C to be $\sim 10^{-10}cm^2\ s^{-1}$; the SIMS measurements, on the other hand, arrive at a value of $4 \times 10^{-15}cm^2\ s^{-1}$.[6] In an attempt to resolve this apparent discrepancy between chemical and electronic measurements, we have extended our experiments on the effects of deuterium plasma treatment to germanium, in which even greater defect neutralization depths are observed than in silicon. We describe attempts to separate the various dynamic features of plasma exposure, compare SIMS measurements on plasma deuterated germanium samples to DLTS measurements on the same material, utilize an electrolytic method of hydrogen incorporation which does not produce surface damage and propose a method to unambiguously determine the hydrogen profile in plasma-treated samples at a much higher sensitivity than is possible by SIMS. We conclude that diffusion of atomic hydrogen into the bulk of our samples, and its subsequent reaction with defects, is the cause of the defect neutralization observed after hydrogen plasma exposure.

Experimental

The germanium used was high-purity p-type material ($N_A - N_D = 2 \times 10^{11} cm^{-3}$) grown in these laboratories from silica crucibles under one atmosphere of H_2. For DLTS measurements of defect passivation depths, 2 mm thick slices were plated with either copper or nickel, and diffused for eight to ten hours at 450°C (copper) or 600°C (nickel) to produce uniform doping. Samples were withdrawn rapidly from the furnace at the completion of the diffusion to avoid precipitation of the copper and nickel. After etching the samples, contacts were fabricated by implanting 25 keV ^{11}B ions in one face, and 25 keV ^{31}P ions in the opposite face, both at a dose of $10^{14} cm^{-2}$. After an appropriate annealing cycle (maximum temperature 330°C), this procedure formed thin (0.1 μm) stable p^+ and n^+ contacts respectively. The full area slices were diced into 5 x 5 mm^2 diodes. For SIMS measurements, Syton polished wafers were diced into 3 x 3 mm^2 samples before exposure to the plasma.

The hydrogenation system is shown schematically in Fig. 2. High-purity deuterium gas (or helium, in some experiments) was passed through a quartz tube at low pressure (0.1 - 0.5 torr); the vacuum system included a LN_2 trap to prevent backstreaming of pump oil. Plasmas were created by coupling 13.56 MHz RF power (300 W) to the tube via a copper coil, while the samples were heated on a graphite block to which 450 kHz RF power was coupled. The temperature of the sample was monitored by a pyrometer, while the pressure in the tube was measured by a capacitance manometer.

DLTS measurements were performed in a system based on a 1 MHz Boonton 72B* capacitance bridge, and an electronic correlator[16]. Thermal scans were achieved by placing the samples in a cryostat cooled by a CTI Model 21* closed-cycle refrigerator, or by use of a Janis Research Company Model DT* helium exchange gas dewar.

Results

1. Effect of Plasma Gas Species

One explanation for the apparent discrepancy between chemical and electronic measurement of hydrogen incorporation in semiconductors is that the observed neutralization is not due to passivation of broken bonds by hydrogen. Our hydrogen incorporation occurs in a very complex process, and one must examine the physical characteristics of a hydrogen plasma to determine whether one of the many simultaneously occurring effects could be responsible for the neutralization. Samples heated in a plasma are subject to phenomena such as bombardment of the surface by ions and the absorption of ultraviolet and visible light. To simulate these effects without the presence of hydrogen, we exposed copper- or nickel-diffused germanium samples to helium plasmas, and checked with DLTS to determine if any defect neutralization occurred. Figure 3(a) shows the DLTS spectrum from a copper-diffused germanium sample after exposure to a helium plasma for three hours at 300°C. This spectrum is essentially unchanged from that obtained prior to the helium plasma exposure. The reduction in electrically active defect concentration after heating in a deuterium plasma, however, is obvious from the DLTS spectrum of Fig. 3(b), which was obtained from a comparison section of the material used in Fig. 2(a). To check that this result was not simply a function of the defect species, we performed the same experiment on nickel-doped germanium, as shown in Fig. 3(a) and 3(b). Again, no passivation after exposure to the helium was evident, but heating in a deuterium plasma under the same conditions produced significant neutralization. These results were repeated using gold-doped n- and p-type silicon samples, and once more exposure to a deuterium plasma proved effective

in passivating the E_c - 0.53 eV gold-related acceptor level, and the E_v + 0.35 eV gold-related donor level, just as does atomic hydrogen[11]; exposure to a helium plasma did not affect the concentration or the depth profile of either of the two gold-related levels. The results of these experiments strongly suggest that hydrogen (or deuterium) is directly involved in the neutralization of deep levels.

2. Effect of Plasma Power and Pressure

Additional experiments were carried out on copper-diffused germanium samples as a function of deuterium plasma power and of deuterium pressure. Figure 5 shows the concentration profile of the E_v + 0.33 eV Cu^{2-} level in germanium for two different power levels of the plasma, at constant deuterium pressure (0.1 torr). At the high power level (300 W) the neutralization of the Cu^{2-} is more effective (more complete) than at the lower power level (60 W). This result is justification for using helium plasmas in the previous section, because the efficiency of defect neutralization is not highly sensitive to the power density, and hence resulting velocity distribution in the plasma. In short, the helium plasma is dynamically similar to the deuterium plasma, except for the presence of the deuterium. Figure 6 shows the concentration profile of the Cu^{2-} level for two different plasma pressures (0.1 and 0.5 torr) at constant plasma power (300 W). In this case there is a similar degree of neutralization, but to a greater depth in the plasma exposure carried out at higher pressure (0.5 torr). Thus the efficiency and depth of defect passivation depend slightly on the plasma parameters. That increasing the temperature of the sample during the plasma exposure leads to more efficient neutralization to greater depths has been reported earlier[8,11,12].

3. SIMS Measurements

The depth profiles of deuterium incorporated into single crystal germanium samples were measured by SIMS using a commercial Cameca IMS 3f* system[17]. Cesium ion bombardment was used to sputter the plasma treated surface, and the depth scale was established from the crater depth at the completion of the measurements. Ion implanted standards provided a calibration for absolute concentration determinations. Figure 7 shows a set of deuterium profiles in germanium as a function of the temperature of the sample during the plasma exposure--each plasma treatment was carried out for one hour (300 W, 0.1 torr). It is interesting to note that as in the case of silicon[6], the penetration of deuterium is confined to the near surface region. A fit of any single function to the profiles measured does not lead to a deuterium profile extending to depths of 80 μm. Indeed, as measured by SIMS, the incorporation depth of deuterium after heating in the molecular gas at 900°C (close to the melting point of germanium, Tm = 936°C) for one hour was comparable to that attained by heating in a deuterium plasma at 800°C for the same time.

As well as the diffusivity of hydrogen, we need to consider its solubility. The solubility of hydrogen in germanium at the melting point is ~ $10^{15} cm^{-3}$.[18] The measured concentration of hydrogen in the near surface region after plasma hydrogenation at much lower temperatures exceeds the bulk solubility near the melting point by a factor of 10^3. This is indicative of damage which enhances the solubility. Previous measurements of hydrogen diffusion through single-crystal silicon[19] and tritium outdiffusion from silicon[20] have yielded diffusion coefficients of hydrogen high enough at 250 - 400°C to explain the DLTS measurements of neutralization of defects after plasma processing. As well, Seager _et al_ have observed deep bulk diffusion of atomic hydrogen in silicon[7]. The point of this is simply that the SIMS measurements on plasma-

treated samples may be irrelevant to the bulk concentrations of hydrogen. It seems clear that there is significant plasma-induced damage after glow discharge exposures. Channelling measurements performed using 1.5 MeV α particles were unable to detect any surface damage on samples exposed to the deuterium plasma at low temperatures (< 700°C) but for T $\geq$ 750°C we observed severe plasma etching of germanium, possibly due to the formation of volatile Ge-H compounds which are more easily sputtered than germanium itself. At 900°C plasma exposures the surface is severely etched; below 750°C there is no damage visible under 50x magnification.

4. Maximum Defect Densities Neutralized in Deuterium Plasmas

In an attempt to directly compare the density of recombination centers neutralized after plasma treatment with the near surface deuterium profile measured by SIMS, we increased the copper concentration in doped germanium samples to levels above the detection limit of SIMS for deuterium.

Slices of gallium-doped germanium (8×10^{14} - $2 \times 10^{15} cm^{-3}$) were plated with copper to a surface density of $6 \times 10^{19} cm^{-2}$. The 2 mm thick slices were then diffused for two hours at 700°C to uniformly dope the material; the solid solubility of copper[21,22] at this temperature is ~ $4 \times 10^{15} cm^{-3}$. A blocking contact was fabricated on the slices by diffusion of antimony from a vapor source with the sample held at ~ 700°C for one hour[23]. This formed a thin (~ 2.1 μm) stable n^+ contact.

The slices were cut into 2 x 2 mm^2 samples. Some were heated for one hour at 700°C in a deuterium plasma (300 W, 0.5 torr), some at the same conditions in molecular deuterium. All of these plus several blank samples from the same copper-diffused slice, were heated to 750°C for five minutes in a separate furnace, then rapidly quenched to room temperatures by dropping

into a container of ethylene glycol. The quench time was of the order of 3 – 5 seconds. After masking the n^+ contact and etching all other surfaces, palladium was evaporated onto the rear face to provide an ohmic contact.

DLTS scans on the blank samples, and those heated in molecular deuterium proved to be identical within the error of results obtained from five samples of each type. Figure 8(a) shows that the diffusion and heat cycles were successful in quenching in doubly ionized copper levels to a concentration of $1 \times 10^{15} cm^{-3}$, uniform over the region investigated (~ 1.6 μm from the antimony contact, i.e. at a depth within the samples of ~ 3.7 μm). Samples which had been heated in the deuterium plasma showed average concentration of the Cu^{2-} level of only ~ $6 \times 10^{14} cm^{-3}$, reaching a minimum of $4 \times 10^{14} cm^{-3}$, also uniform over the region investigated [Fig. 8(b)]. These results indicate that neutralization is incomplete above a certain deep level concentration, which in turn shows that there must be a minimum deuterium concentration present. Unfortunately, this minimum concentration is below the detection limit of SIMS. This minimum concentration of deuterium further indicates that the deuterium profile must have an extended "tail", strongly deviating from a simple complementary error function. Attempts to produce even larger electrically active concentrations of copper by heating at higher temperatures were unsuccessful—the maximum concentration of Cu^{2-} levels we could attain was $1 \times 10^{15} cm^{-3}$ and we were unable to neutralize these to a lower density than $4 \times 10^{14} cm^{-3}$.

5. Electrolytic Doping

As pointed out by Oehrlein *et al*[24], the high concentration (~ $10^{20} cm^{-3}$) of hydrogen that can be incorporated in silicon by ion implantation is indicative of damage-enhanced solubility. We propose that the same situation exists in

plasma-treated samples. Therefore methods of introducing hydrogen which do not also produce lattice damage are desirable. We attempted to provide a "cold" source of atomic deuterium by evaporating successive layers of vanadium and palladium onto the germanium surface, then heating in molecular deuterium at 300°C. The metal layers may store large amounts of atomic deuterium[25,26], and we attempted to use these layers as a source of deuterium for diffusion into the bulk of the sample (the vanadium is less reactive with the germanium than palladium). The procedure was unsuccessful, probably due to the problem of transferring the deuterium across the metal-semiconductor interface. This viewpoint was supported by the fact that even heating in a deuterium plasma produced no noticeable hydrogen incorporation in the germanium, as evidenced by DLTS measurements. Similar problems were experienced with the formation of palladium silicides on silicon samples electrolytically deposited with hydrogen at room temperature, with the silicides acting as barriers to diffusion of the hydrogen[24].

An electrolytic method which was successful in introducing hydrogen into germanium consisted of using phosphoric acid as the electrolyte. The copper-doped sample with implanted contacts was made the cathode of the electrolytic cell while a graphite rod served as the anode. Ortho-phosphoric acid (H_3PO_4) converts to the stable pyro configuration ($H_4P_2O_7$) at 213°C allowing charging of the germanium sample with hydrogen at temperatures similar to the ones used during plasma processing. Typically the cell was run for three hrs at 200 - 280°C at a current density of 0.1 A/cm^2. Figure 9 shows the DLTS spectra of samples electrolyzed at 200°C and 280°C respectively for three hrs, while Fig. 10 shows the concentration profile of the Cu^{2-} centers after such treatment. The results are identical to those achieved by plasma hydrogenation for the same conditions. Since there is no surface damage produced by the electrolytic

charging, nor are there any other energy deposition processes as in the plasma, we believe that hydrogen passivation of the defect states is the only reasonable explanation, i.e. the atomic hydrogen does achieve significant bulk diffusion at temperatures of ~ 300°C in both processes--plasma exposure as well as electrolytic hydrogen generation.

Discussion

The work of Frank and Thomas[27] involving high temperature (800 - 910°C) measurements of the diffusion coefficient of hydrogen in germanium yielded the relation:

$$D_H = 2.7 \times 10^{-3} \exp(\frac{0.38 \text{ eV}}{kT}) \ (\text{cm}^2 \text{ s}^{-1}) \quad (1)$$

Thus, at 300°C, $D_H = 1.2 \times 10^{-6} \text{cm}^2 \text{ s}^{-1}$. However, a later indirect measurement by Hall and Soltys[28] at 430°C yielded $D_H \sim 2 \times 10^{-8} \text{cm}^2 \text{ s}^{-1}$. They attributed much of the difference as being due to hydrogen molecule formation at the lower temperatures with a consequent reduction in the effective diffusivity of the hydrogen. At 300°C we have previously estimated $D_H \sim 3.5 \times 10^{-9} \text{cm}^2 \text{ s}^{-1}$ from DLTS-hydrogenation experiments[8], in fair agreement with the result of Hall and Soltys[28]. We also note that interaction of the hydrogen with defects present in the bulk, or created at the surface by the plasma could further reduce the effective diffusivity. A similar situation holds for silicon, where hydrogenation experiments performed at low temperatures (<400°C) yield values of hydrogen diffusivity[11,29] lower than values extrapolated from high temperature diffusion data[20], and molecule formation and trapping of the hydrogen at defects have been identified as the causes[30]. No special mechanism such as ionization-enhanced diffusion of the hydrogen[31,32] is required to explain the incorporation depths after plasma treatment.

The solubility of hydrogen in germanium[27] at one atmosphere is:

$$S_H = 1.6 \times 10^{24} \exp(-\frac{2.3 \text{ eV}}{kT}) \text{ cm}^{-3}$$
$$= 3 \times 10^{14} \text{cm}^{-3} \text{ at } 900^\circ\text{C} \quad (2)$$

A more refined experimental determination[18] gave a value of 1.2×10^{15}cm^{-3} at 936°C. Extrapolating the Frank and Thomas[27] data to 300°C gives $S_H = 10^4$cm^{-3}. Again, a similar result holds for silicon, where high temperature measurements give extrapolated low temperature values up to nine orders of magnitude below the defect neutralization concentrations observed in DLTS-hydrogenation experiments[19,20]. The significantly enhanced solubility of hydrogen at low temperatures in these materials must be caused by the number of defect or impurity sites available for incorporation of the hydrogen. It has been previously noted in germanium that any acceptor site or strain center has the potential to attract and trap hydrogen[33]. The low temperature (< 400°C) diffusivity and solubility of hydrogen in germanium containing varying concentrations of defect sites could be determined by using tritium plasmas and the self-counting radiation detector technique[18,34]. While the detailed reaction and bonding mechanism of hydrogen with defect states in crystalline semiconductors is somewhat unclear, we can conclude that the diffusion of the atomic species from a plasma to neutralize broken bonds related to these defects has experimentally been established.

Acknowledgments

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Figure Captions

Fig. 1. Apparent diffusion profiles of hydrogen incorporated in silicon by plasma processing for one hr and 350°C, as measured directly by SIMS, and indirectly by DLTS measurements of the passivation of point defects. The dotted line represents a possible hydrogen profile which would be consistent with the results obtained by the two techniques.

Fig. 2. Schematic of the hydrogenation system used. Q is the quartz tube, G the graphite block on which the sample is mounted, C1 is a copper coil which couples 450 kHz RF power to heat the graphite block, C2 is a copper coil which couples 13.56 MHz RF power to generate the plasma, and P is an optical pyrometer for measuring the sample temperature.

Fig. 3. DLTS spectra taken at the same spectral conditions from copper-diffused germanium samples, (a) after exposure to a 300 W, 0.1 torr helium plasma for three hours at 300°C. This spectrum is identical to that of an unheated sample; and (b) after exposure to a 300 W, 0.1 torr deuterium plasma for three hours at 300°C, showing neutralization of the deep copper-related defects. Reverse bias V_R = 5 V, correlator time constant T_c = 10 ms for both spectra.

Fig. 4. DLTS spectra taken under the same conditions as Fig. 2 for nickel-doped germanium samples, (a) after exposure to a helium plasma for three hours at 300°C, (b) after exposure to a deuterium plasma for three hours at 300°C, again showing that the presence of deuterium is required to neutralize the deep-level centers.

Fig. 5. Concentration profile of the E_v + 0.33 eV Cu^{2-} level in germanium as a function of the plasma power, at constant plasma pressure

(0.1 torr). An increase in the RF power level coupled to the gas leads to an increased passivation efficiency of the deep level centers.

Fig. 6. Concentration profile of the $E_V + 0.33$ eV Cu^{2-} level in germanium as a function of deuterium plasma pressure, at constant plasma power (300 W). At higher pressures (0.5 torr), there is an increased depth of neutralization compared to lower pressures (0.1 torr).

Fig. 7. Depth profiles of deuterium in single crystal germanium determined by SIMS, as a function of the temperature of the sample during the plasma exposure. All anneals were one hour in duration, unless otherwise indicated. Differences in the surface concentration are not fully understood, but may be related to variations in damage induced by the plasma exposure.

Fig. 8. DLTS spectra of copper-diffused germanium after, (a) heating in molecular deuterium at 700°C for one hour; and (b) deuterating at 700°C for one hour. Both samples were then rapidly quenched from 750°C in a separate furnace in order to activate as much copper as possible. The maximum density of Cu^{2-} levels neutralized by deuterium was $\sim 5 \times 10^{14} cm^{-3}$ at a depth of ~ 3.7 μm into the sample.

Fig. 9. DLTS spectra taken under the same conditions (reverse bias V_R = 2 V, correlator time constant T_C = 10 ms) for copper-doped germanium heated in an electrolytic bath containing phosphoric acid: (i) three hrs, 280°C with no current being passed in the cell; (ii) three hrs, 280°C at a current density of 0.1 A/cm^2; and (iii) three hrs, 200°C at a current density of 0.1 A/cm^2.

Fig. 10. Concentration profiles of the Cu^{2-} level for the samples in Fig. 9. Only in the samples where atomic hydrogen was evolved at the surface during heating was there neutralization of the Cu^{2-} levels.

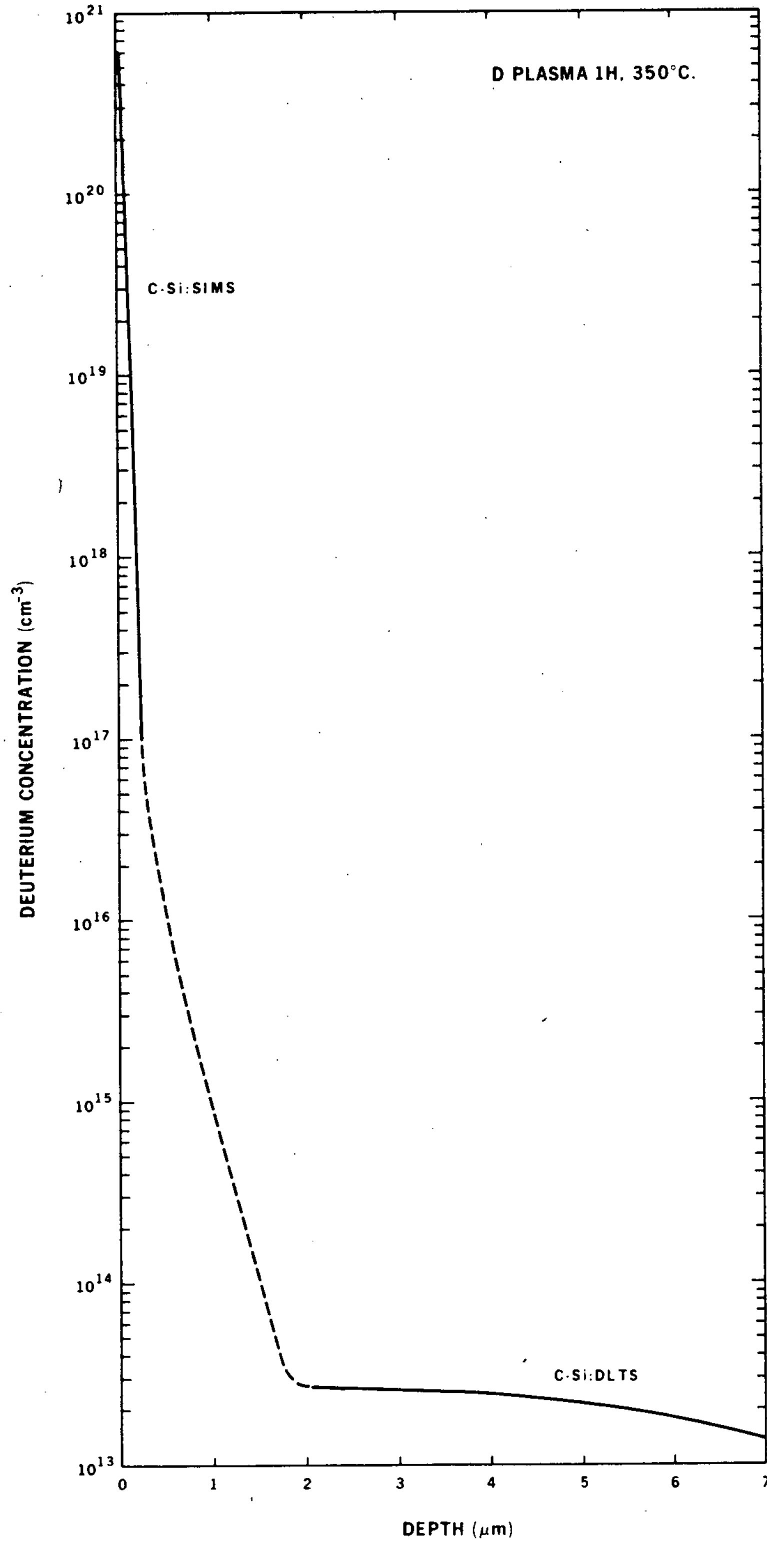

Figure 1.

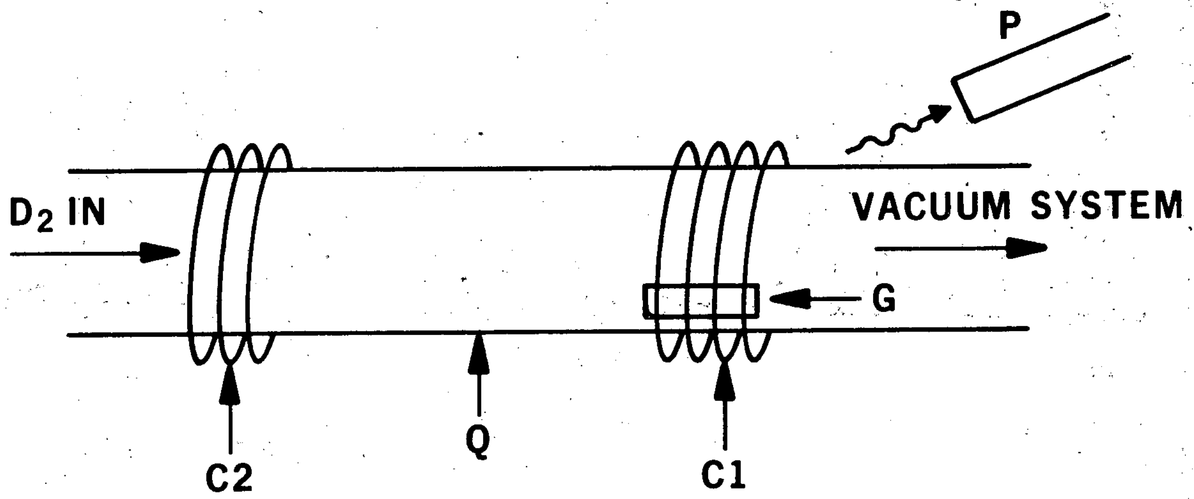

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Figure 2.

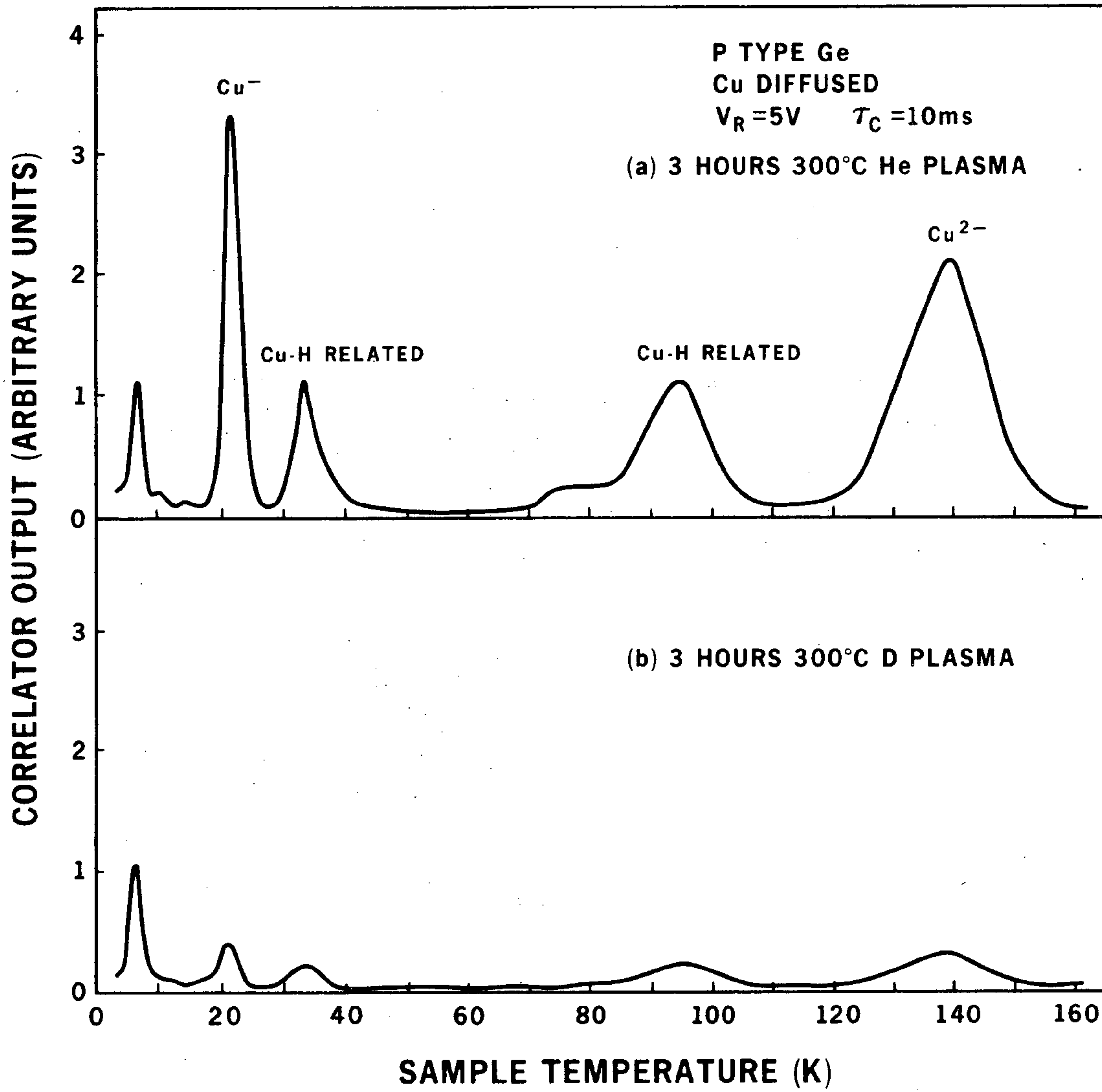

Figure 3.

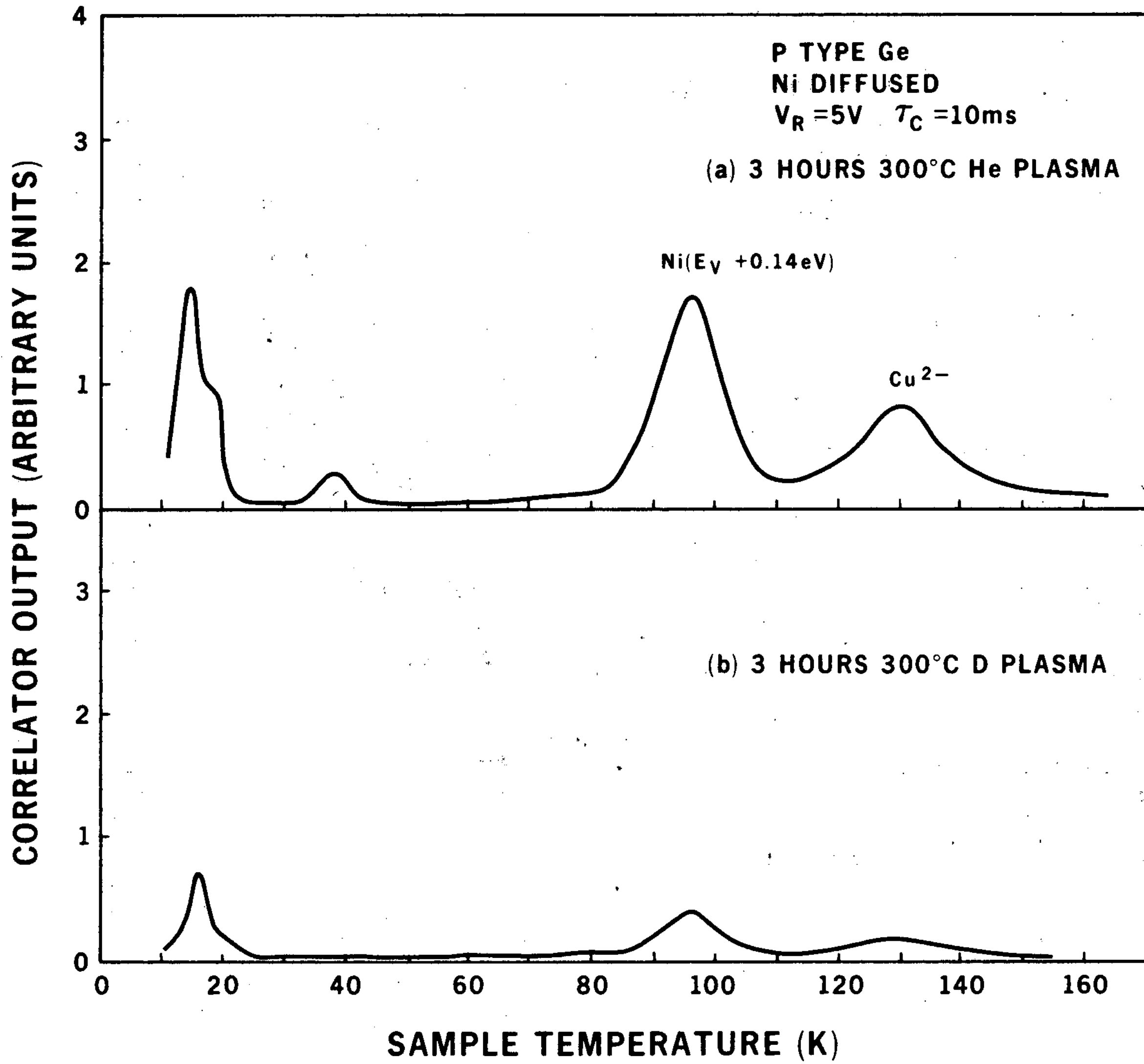

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Figure 4.

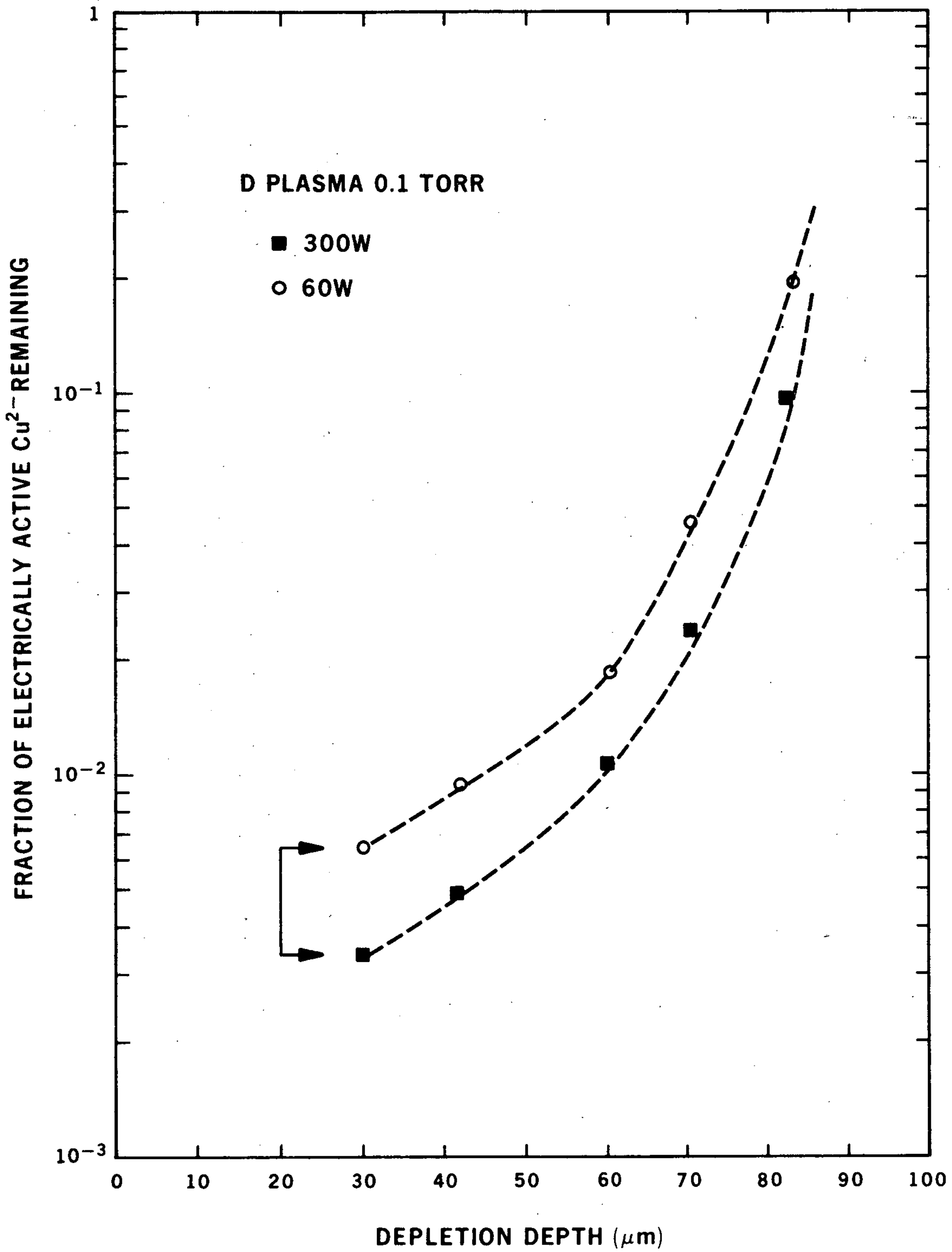
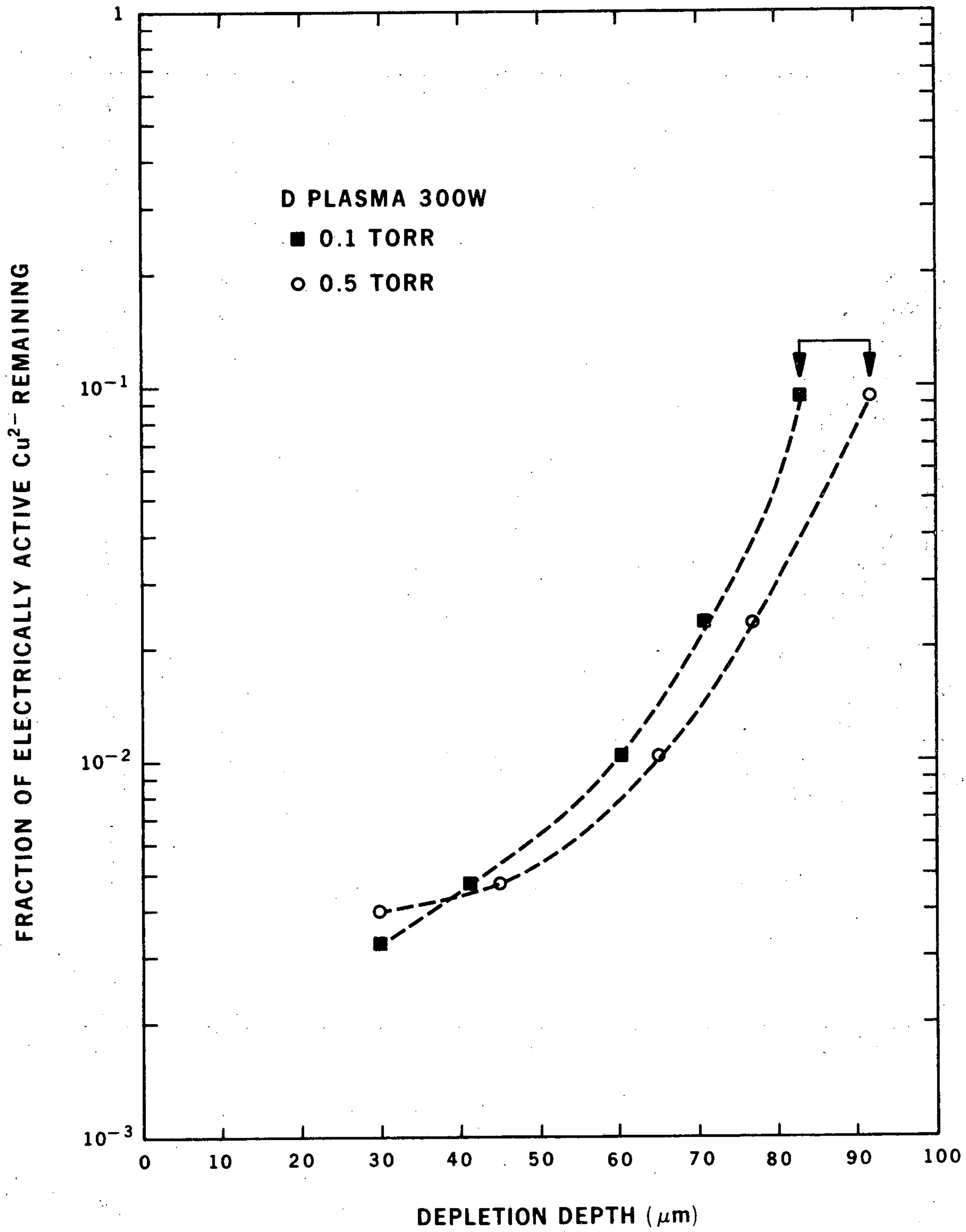


Figure 5.



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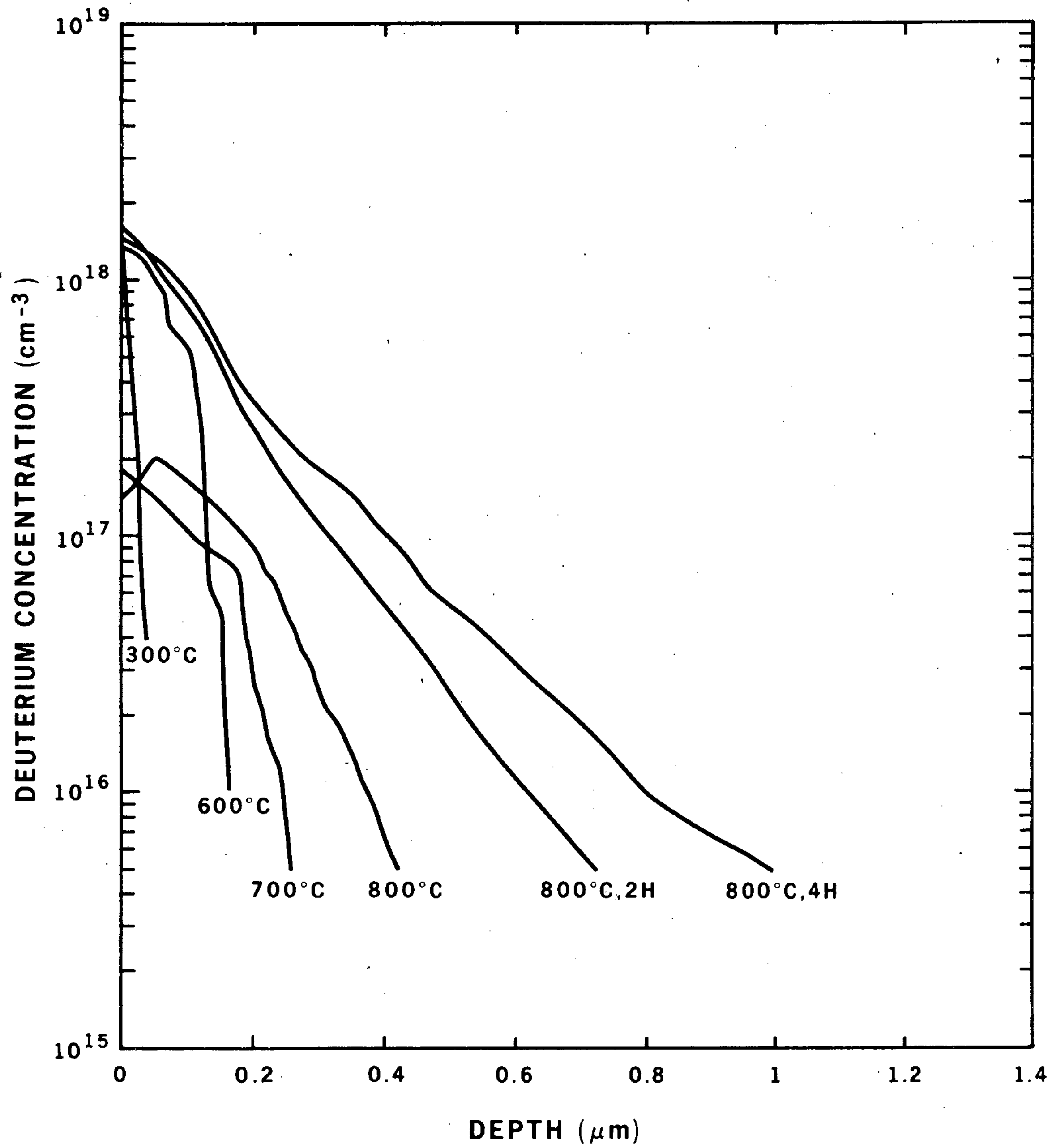

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Figure 7.

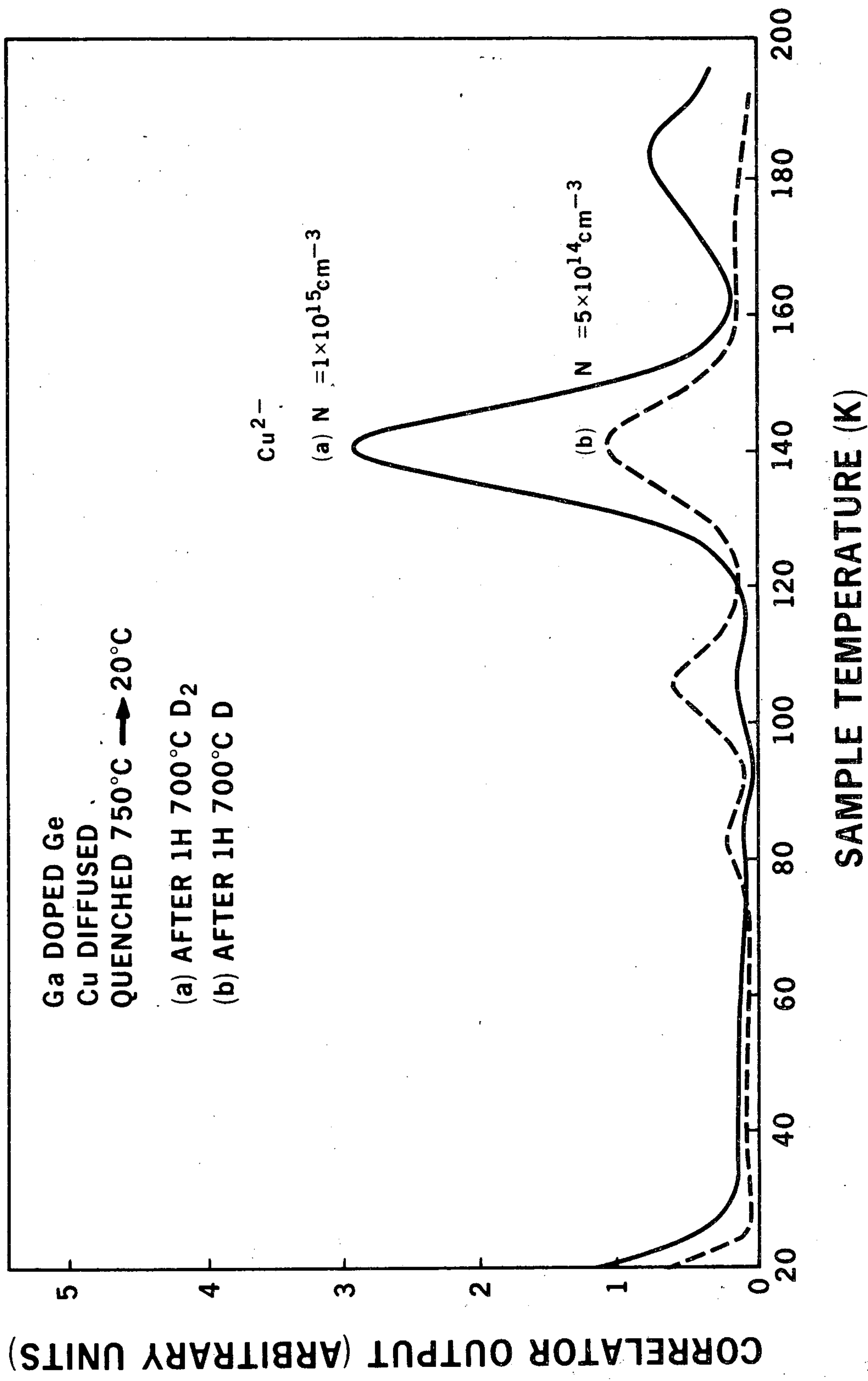

Figure 8.

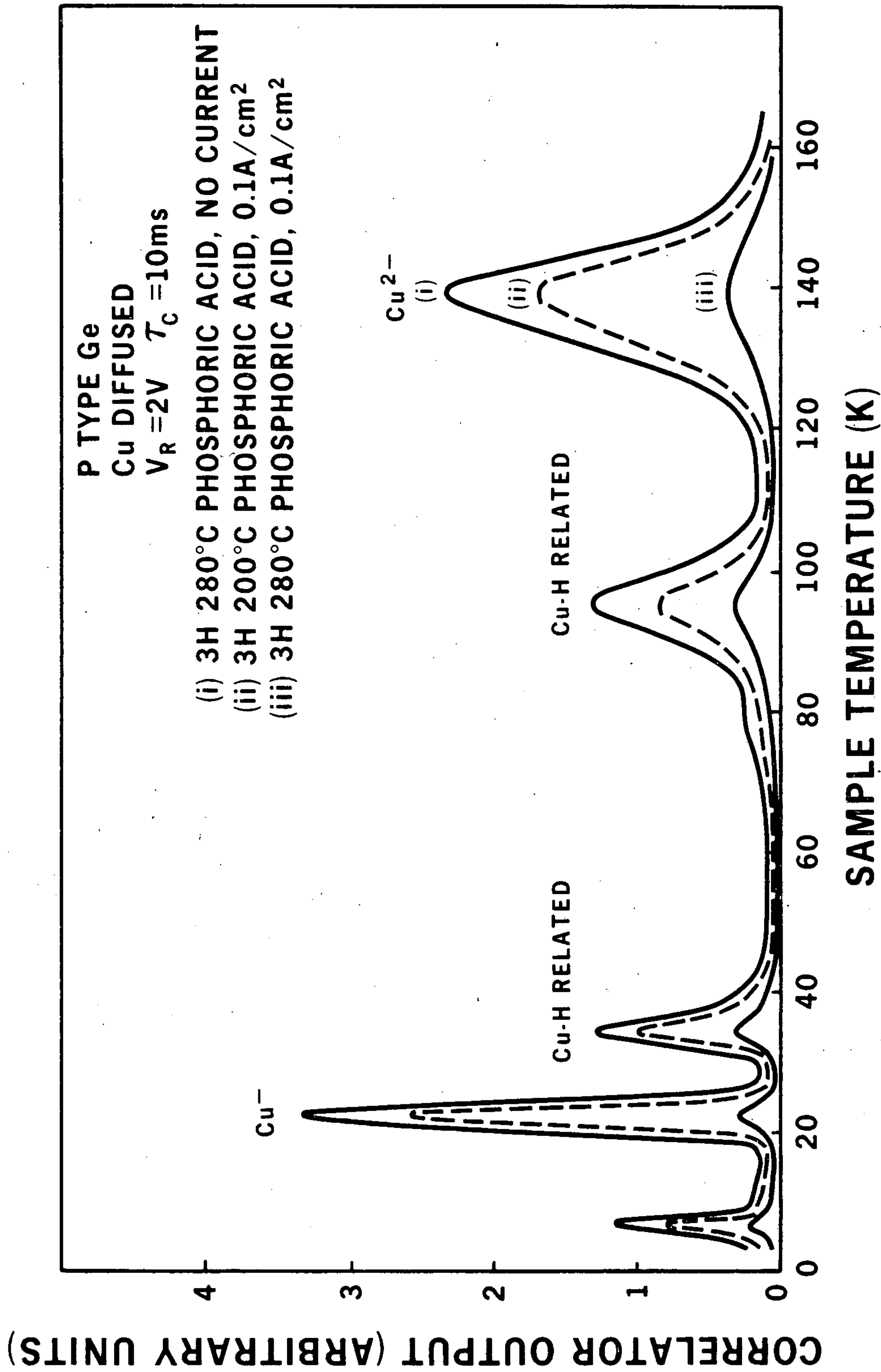

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Figure 9.

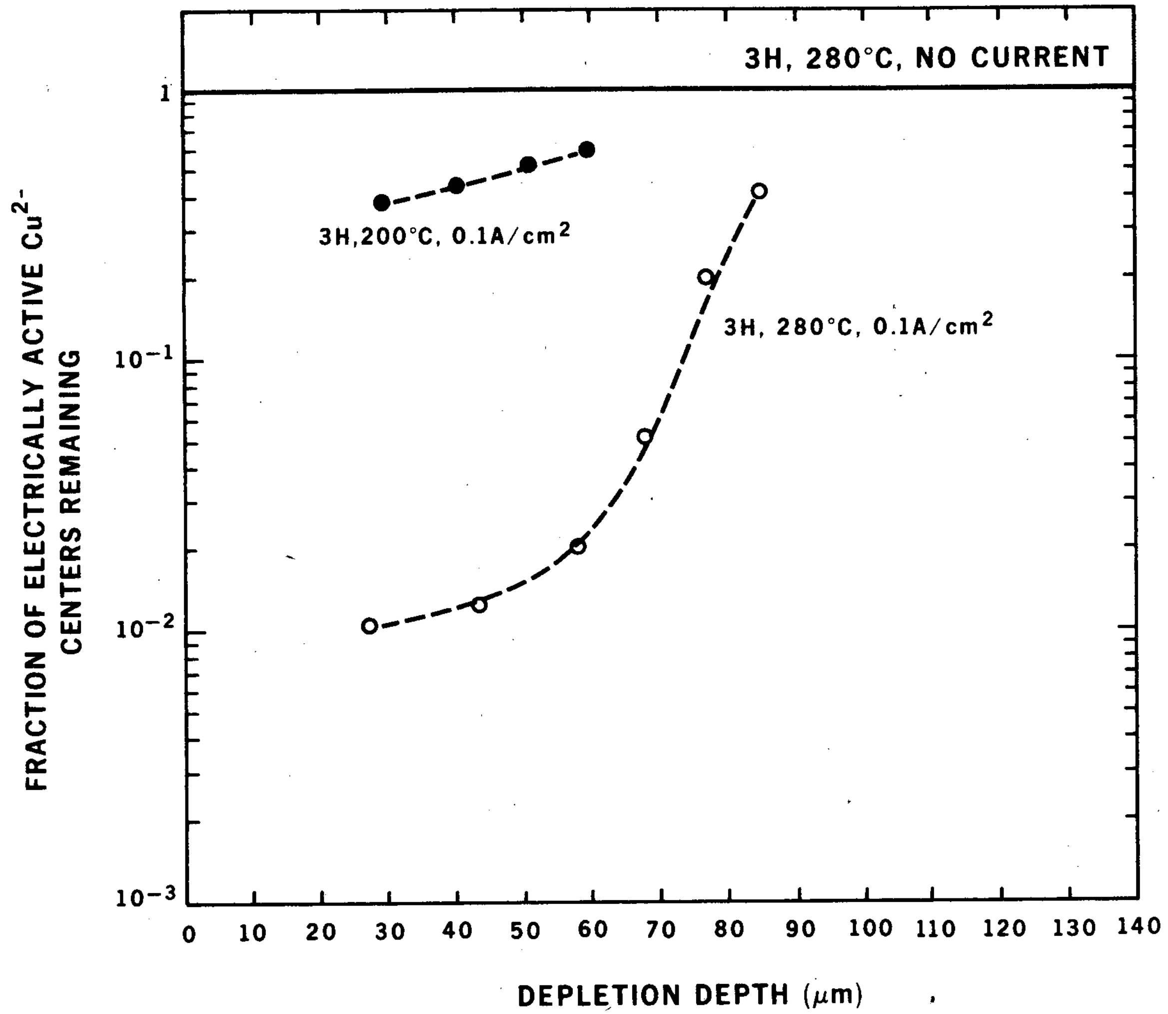

Figure 10.

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