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September 1983

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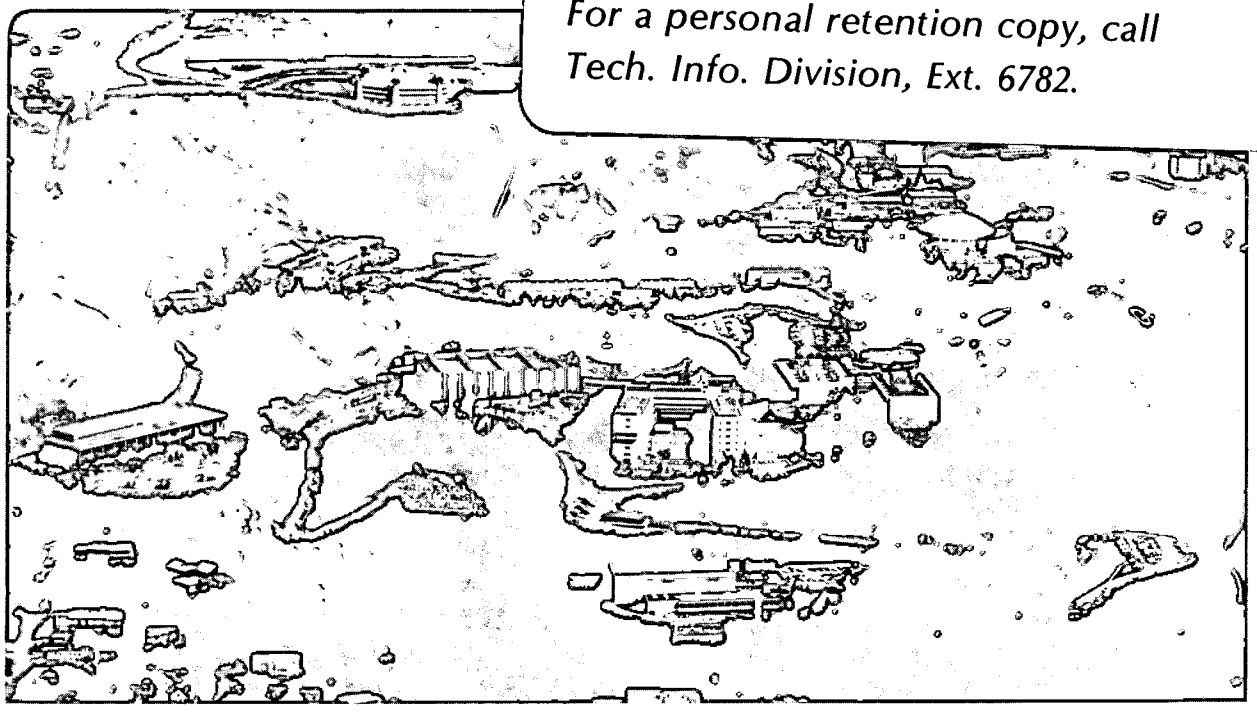

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BULK ACCEPTOR COMPENSATION PRODUCED IN P-TYPE SILICON AT NEAR-AMBIENT TEMPERATURES BY AN H_2O PLASMA

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Bulk acceptor compensation produced in p-type silicon at near-ambient temperatures by an H_2O plasma

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(Received

We report the neutralization of the shallow acceptors boron and gallium in p-type silicon to a depth > 1 μm after exposure to a H_2O plasma for three hours at temperatures as low as 80°C. Uncompensated n-type silicon is unaffected by the plasma treatment excluding donor formation. Exposure to either O_2 or H_2 plasmas does not lead to acceptor removal; however, sequential treatment in an O_2 plasma followed by an H_2 plasma produces the same effect as the H_2O plasma while the inverse sequence has no effect. Our observations can be explained with a model considering rapidly diffusing atomic oxygen and hydrogen which recombine on acceptor sites forming neutral A^-OH^+ complexes. The model shows that acceptor compensation kinetics is dominated by the diffusion of atomic hydrogen.

PACS numbers: 52.40.Hf, 61.70.Wp, 73.30.+y

Interest in positive charge effects upon electron injection into p-Si MOSC devices has recently been revived due to the discovery of a bulk compensating donor [1]. When electrons are injected either by electron beams or by avalanche, a "turn around" [2] of the flatband voltage shift is observed which is due to the generation of positive charge. It had been concluded [3, 4, 5] earlier that SiOH which resides at the SiO_2-Si interface becomes positively charged as a result of electron irradiation and is responsible for the positive charge observed. Sah, et al. [1] have shown that if the oxide is removed and a Schottky junction is formed on the same surface as was subject to electron injection, capacitive transient analysis shows that positive charge is due also to a shallow bulk compensating donor.

In a recent paper, Sah et al. [6] have attributed acceptor compensation in boron-doped silicon to the formation of B^-H^+ pairs. However, in numerous studies [7-11] of defect compensation in silicon using atomic H from plasmas or electrolysis, shallow acceptor compensation has never been observed.

In order to identify the species responsible for acceptor compensation, boron-doped silicon samples were immersed in various RF-induced plasmas at low temperatures. The samples used are either Czochralski grown (oxygen$\sim 10^{18}$ cm^{-3}) or float zone grown (oxygen $< 10^{15}$ cm^{-3}) and are attached with In-Ga eutectic solder to an aluminum plate in a two-inch diameter silica tube for plasma exposure. The plasma is generated by a 13.56 MHz oscillator with an input power of 10 to 300 W. Typical exposure conditions are three hours at 0.5 Torr. The sample temperature during

exposure is measured by a thermocouple inserted into the aluminum plate. By controlling the RF power and by forced air cooling of the plasma tube, exposure temperatures as low as 80°C could be achieved. After plasma exposure, small Al dots are evaporated through a metal mask for Schottky junction formation on the samples.

The net acceptor concentration of the Schottky diodes is probed from the surface inward using a Miller profiler [12]. High and low oxygen concentration samples exposed to an O_2 or H_2 plasma at 145°C for three hours showed no changes in net acceptor concentration when measured at 300K. However, samples exposed to an H_2O plasma showed acceptor removal qualitatively similar to that seen using electron injection. Figure 1 shows the acceptor concentration for three-hour exposures at 84°C and 145°C and for an untreated diode. The results are indistinguishable for both high and low oxygen samples. In sharp contrast no changes are observed when uncompensated n-type samples are exposed to the H_2O plasma.

The annealing behavior of the compensated acceptor center is shown in Figure 2. Dissociation of the neutral center begins below 150°C and is complete when heated to 185°C for 1 hr. These data also imply that significant dissociation must occur during the plasma exposure at 145°C. The dissociation temperature for the neutral center produced by exposure to H_2O plasma is similar to the temperatures found by Sah, et al. [1], for the dissociation of the neutral center produced by electron injection into MOSC devices.

The diffusion constant of the compensating center is found using [15]:

$$N_x = N_s \operatorname{erfc}(x/2\sqrt{Dt})$$

where N_s is the surface concentration and N_x the concentration at x cm of the compensating center and t is the time in sec. Excellent fits to the error integral can be achieved for each sample when $N_s = N_A$. The resulting large values for D suggest a rapidly diffusing interstital species. An attempt was made to compare D_X with literature values for the hydrogen diffusion coefficient D_H but those data were found to be too widely scattered to be useful. Consequently, new measurements of D_H were made in the temperature range of interest. This was done by saturating silicon samples at 1000°C with Au ($N_B = 3x10^{16}$, $N_{Au} = 3x10^{15}$), exposing these to a H plasma and measuring the change in Au donor concentration with DLTS [13]. The exposure time to H plasma was selected to minimize the errors in determining D_H. D_H is found using [14]:

$$X = 5.4 \sqrt{D_H t}$$

where X is the depth at which $Ns/Nx > 10^3$. Table I summarizes the results for D_X and D_H.

The data of Table I are plotted in Figure 3 together with a room temperature value determined by electrolysis [15]. Also shown are curves for D_H extrapolated from high temperature (800-900°C) atomic H diffusion [16] and from lower temperature (400-500°C) tritium out-diffusion [17]. The errors in determining D_H by Au donor compensation are much larger than those in D_X due to the uncertainty in N_{Au} and X. An estimate of these errors is given in Figure 3.

The results presented in Figure 3 lead to the following conclusion: (1) high temperature atomic hydrogen diffusion data [16] cannot be extrapolated to low temperatures, (2) tritium out-diffusion [17] below

500°C adequately represents low temperature H diffusion, (3) the compensating center suffers from dissociation annealing above 100°C but D_X approaches D_H below 100°C. An explanation for these distinct temperature regimes for D_H would be that at high temperature, H_2 is unstable and H diffuses atomically and at low temperatures, H is recombining to H_2 either directly or, more probably, through a recombination center [18].

The nearly identical results for the activation energy for the dissociation of the compensating center upon electron injection [1] and H_2O plasma exposure suggests that the same center is involved in both experiments. This observation is further reinforced by the fact that the electron injection compensation center is always associated with H_2O [1-5].

Summarizing our experimental evidence, we conclude that the compensating center cannot be hydrogen but is most probably the hydroxyl ion OH^+. This conclusion is also compatible with the results of electron injection experiments insofar that OH is an abundant ion in practically all the silica used for MOSC gate insulators.

OH in Si exhibits some similarities to LiO in Si, to OH in Ge [19-21] and to LiO in Ge [22,23]. In all these cases, O assumes the neutral charge state, accepts a positive ion and becomes a shallow donor. However, OH in Si is unique in that free O binds to an acceptor instead of residing in the lattice and thus, the resulting center is only compensating and never becomes a free donor.

The detailed mechanism of the formation of acceptor-OH centers may be explained by the following sequence: if p-Si is first exposed to an O_2 plasma, then the O_2 is pumped away and is replaced by an H_2 plasma, acceptor

compensation is observed just as with an H_2O plasma. The sequence is:

$$A^- + O \rightarrow AO^-$$

$$AO^- + H^+ \rightarrow AOH.$$

This would imply that O diffuses faster than H and that AOH formation kinetics is controlled by the H diffusion rate. H diffuses slower than would be extrapolated from high temperatures because of the reaction:

$$H + H \rightarrow H_2$$

or because of H trapping. It can be concluded, then, that the reaction

$$O + O \rightarrow O_2$$

occurs much more slowly than H recombination or may not occur at all.

The annealing of AOH has kinetics very similar to that of OH in Ge [21] and probably occurs because both involve removing H from a bound O. The dissociation can be described by :

$$AOH \rightarrow AO^- + H^+\uparrow.$$

It will be interesting to explore if the OH compensated acceptor complexes involve "dynamic tunneling" of hydrogen [20].

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FIGURE CAPTIONS

Figure 1. Bulk acceptor compensation as a result of three-hour exposure to an H_2O plasma at 0.5 Torr at the temperatures shown.

Figure 2. Annealing behavior of the compensating center N_D normalized to the bulk acceptor concentration N_A. Initial curve is for 3 hrs. exposure to H_2 plasma at 145°C. $N_A = 9.4 \times 10^{14}$ cm^{-3}. Each curve is for a separate sample annealed for 1 hr. at the indicated temperature.

Figure 3. D_X compared with D_H from various sources. Reference 16 is an extrapolation from atomic H diffusion measured at 800-900°C. Reference 17 is extrapolated from tritium out-diffusion at 400-500°C. Reference 15 is from electrolytic H injection at room temperature.

TABLE I

Summary of Measurements of the Diffusion Constant of the Compensating Donor Complex D_X and for Atomic Hydrogen D_H.

N_A (cm^{-3})	T(C)	D_X (cm^2 sec^{-1})	D_H (cm^2 sec^{-1})
9.4×10^{14}(B)	84	$3.0 \pm .2 \times 10^{-13}$	
9.4×10^{14}(B)	110	$4.5 \pm .2 \times 10^{-13}$	
9.4×10^{14}(B)	145	$5.4 \pm .2 \times 10^{-13}$	
1.8×10^{16}(B)	145	$3.3 \pm .2 \times 10^{-13}$	
3.2×10^{16}(Ga)	145	$3.3 \pm .2 \times 10^{-13}$	
3.0×10^{16}(B)	84		6.7×10^{-13}
3.0×10^{16}(B)	110		3.1×10^{-12}

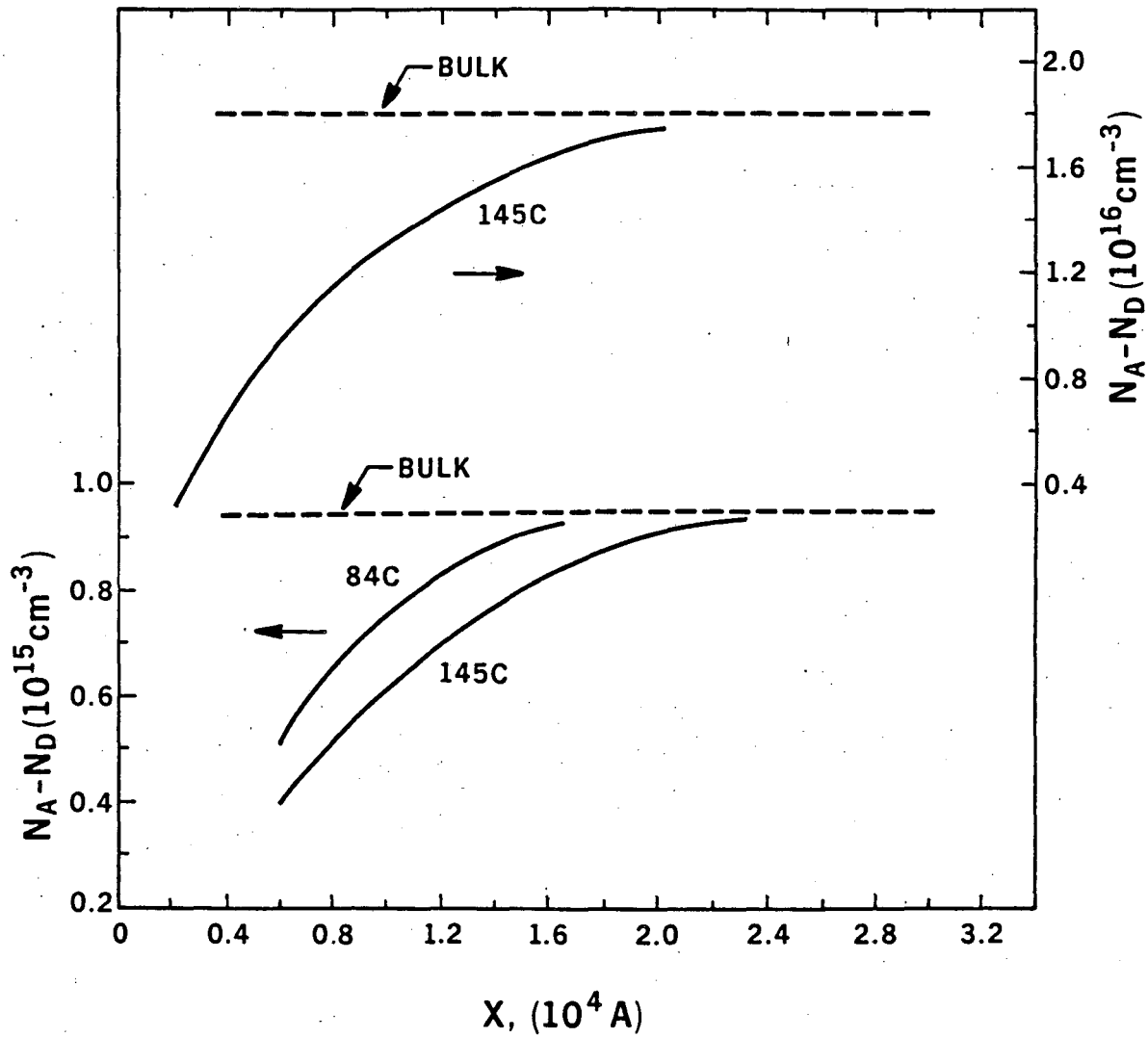

Figure 1.

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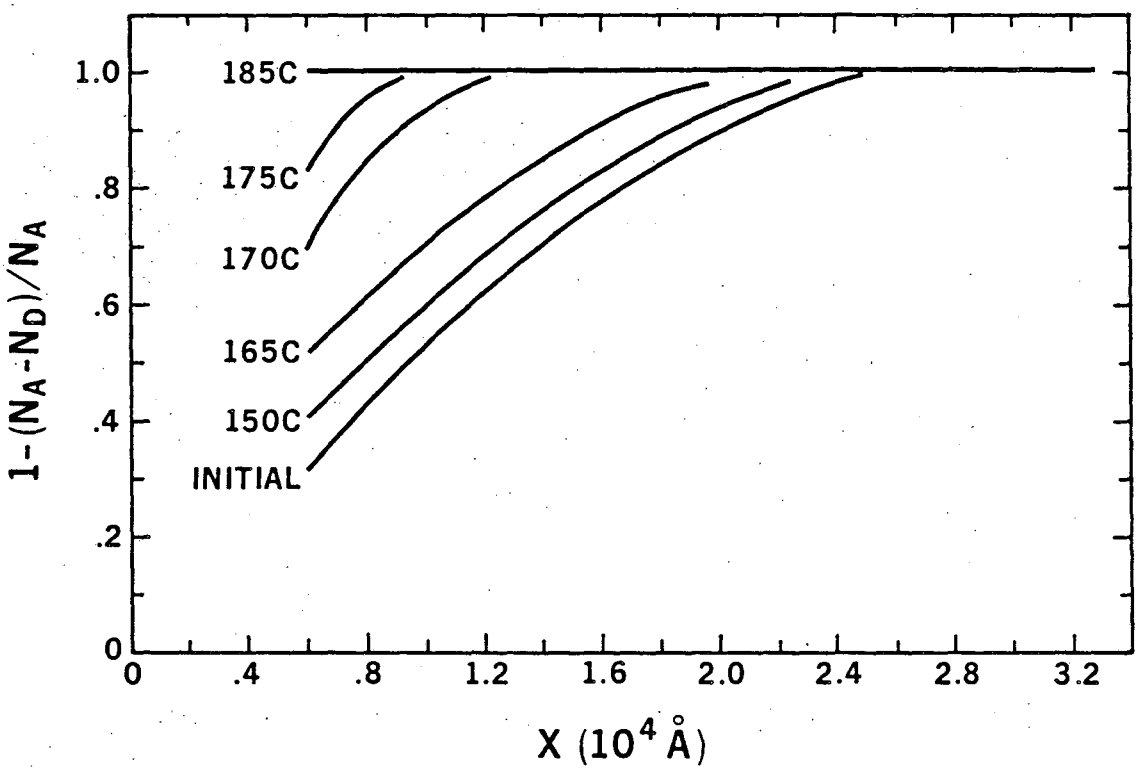

Figure 2.

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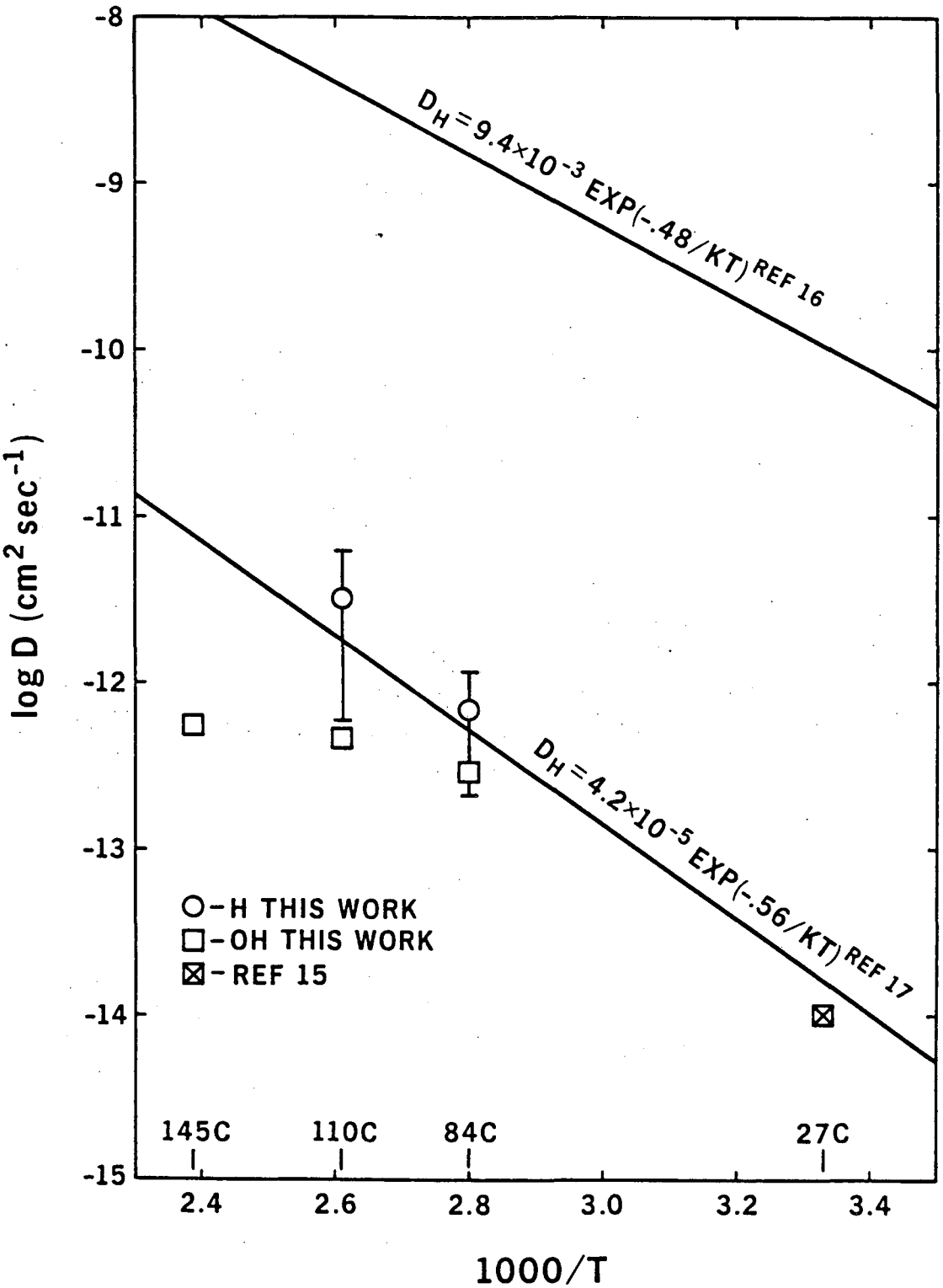

Figure 3.

XBL 839-11889

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