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November 1983

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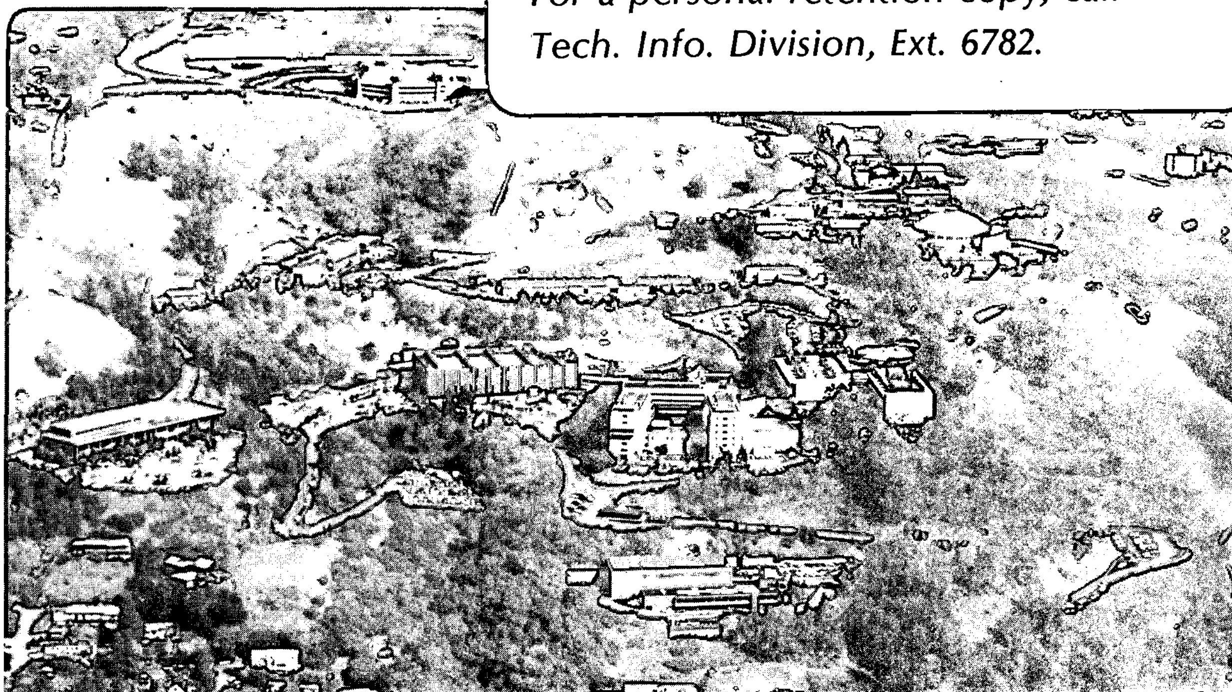

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LOW-TEMPERATURE OXYGEN DIFFUSION IN SILICON

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Low-temperature oxygen diffusion in silicon

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(Received

Using the formation of the proposed neutral acceptor-hydroxyl complex AOH as a marker, the diffusion coefficient of a mobile oxygen species introduced in p-type silicon from a plasma source at near ambient temperatures is determined to be:

$$D_0 = 2.98 \times 10^{-10} \exp(-0.159/kT) \ cm^2 \ s^{-1}$$

At 35°C the diffusion of this unbound oxygen species is 30 times faster than the effective diffusion of atomic H introduced in a similar manner.

An activation energy of 1.60 eV is found for the thermal dissociation of this oxygen species bound to boron.

PACS numbers: 66.30.Jt, 52.40.Hf

The diffusion coefficient of a mobile oxygen species in silicon at near ambient temperatures has been measured using the kinetics of the neutralization of bulk shallow acceptors. In a recent work[1] it was established that: 1) bulk shallow acceptors A are neutralized by OH introduced from a plasma, 2) these acceptors can also be neutralized by first forming an acceptor-oxygen complex AO^- using exposure to an O_2 plasma followed by an H_2 plasma to form a neutral AOH type complex, 3) the oxygen species diffuses faster than H at low temperatures so that the kinetics of neutral AOH complex formation is limited by the effective diffusion of atomic H at these temperatures, and 4) the oxygen species is more strongly bound to the acceptor than H is to the AOH complex.

Using these experimental results, it is possible to determine the diffusion coefficient of the mobile oxygen species in silicon at temperatures inaccessible by the usual methods. p-type silicon samples are first exposed to an oxygen plasma for short times at low temperatures and then to a hydrogen plasma for longer times and/or temperatures so as to saturate any acceptor-oxygen centers with atomic hydrogen and thus produce acceptor neutralization. The sample exposures are always done at $T <$ 100°C to avoid errors due to AOH complex dissociation.

The float-zoned p-type silicon samples ($N_B = 9.2 \times 10^{14} cm^{-3}$) are attached with Ga-In eutectic solder to a temperature-controlled aluminum plate and exposed to a 0.1 Torr O_2 or H_2 plasma in a silica tube excited by a 13.56 MHz RF generator. The plasma exposure apparatus is the same as Ref. 1. Silicon samples (4 x 4 x 0.5 mm) with chemically etched surfaces are exposed to the O_2 plasma for 40 min. at 37°C, 63°C and 84°C and then exposed to an H_2 plasma for 3 h at 84°C. After cleaning in 10% HF and evaporation of Al Schottky contacts (dia. = 2 mm) on the plasma exposed

face, the depth distribution of the acceptor neutralization is determined using a Miller profiler.[2] Error function curves are fit to the compensation profiles using[3]:

$$N_x = N_s \operatorname{erfc}(x/2\sqrt{Dt}) \quad (1)$$

where x is the depth from the surface in cm, t is the plasma exposure time in seconds, D is the diffusion coefficient of the mobile species of oxygen in cm^2s^{-1}, N_x is the concentration cm^{-3} at x and N_s is the surface concentration. Excellent fits to the error integral are found for all samples when $N_s = 5 \times 10^{14} cm^{-3}$. In our previous experiment[1] in which the AOH complexes were formed by H_2O plasma exposure, it was found that $N_s = N_B$ provided the best fit to the measured profiles. The difference in this sequential plasma experiment is not fully understood, but may indicate a non-saturation of the acceptors by the oxygen species or to insufficient oxygen plasma density.

The O_2 plasma contains all the charge states of oxygen and it is not clear which is the rapidly diffusing species--it may be atomic oxygen or the proposed rapidly diffusing O_2 molecule.[4] Figure 1 shows the diffusion coefficient D_0 of the mobile oxygen species as a function of temperature for the samples measured. Also shown is the diffusion coefficient D_H for atomic hydrogen as determined in Ref. 1. We stress that D_0 is the diffusion coefficient of an unbound atomic or molecular oxygen species introduced from the plasma and should not be confused with bond-centered interstitial oxygen already in the crystal. There is no significant difference in low temperature acceptor neutralization for Czochralski or float zone silicon samples.

The activation energy for the thermal dissociation of the A-O complex is found by first exposing a p-type silicon sample to an O_2 plasma,

heating for a short time at a higher temperature and then exposing to an H_2 plasma at a lower temperature to produce AOH neutral complexes from any remaining AO.

Figure 2 shows the resultant acceptor profiles for separate samples which were first exposed to an O_2 plasma for 1 h at 110°C, heated for 5 min at the indicated temperature and then exposed to an H_2 plasma for 3 h at 110°C. For temperatures below 150°C, the profiles are identical. The activation energy for dissociation is found using[5]:

$$\frac{N}{N_0} = \exp - \left[t\nu \exp^{-(E_D/kT)} \right] \tag{2}$$

where N/N_0 is the integrated fraction of AO-type complex remaining, E_D is the dissociation energy, and ν is the dissociation attempt frequency.

Figure 3 shows the experimental points derived from Fig. 2. An excellent fit of Eq. (2) to the data is obtained using $\nu = 10^{14}\ s^{-1}$ and E_D = 1.60 eV. By comparison, $E_D \simeq 1.0$ eV for the AOH-type complex,[6] i.e., the oxygen species is bound more strongly to the acceptor than is H bound to the AO center.

The diffusion behavior of the mobile oxygen at low temperatures is peculiar in that both the activation energy for diffusion of 0.159 eV and the pre-exponential factor of $2.98 \times 10^{-10}\ cm^2\ s^{-1}$ are much smaller than for any known impurity atom in silicon. It is difficult to imagine any diffusion enhancement mechanism[7] which could have sufficient effect at these low temperatures. Enhancement effects from the O_2 plasma such as e-h generation from light or excess point defect generation from oxidation should be insignificantly small effects. One effect which is possibly important is ion bombardment generation of excess point defects due to the plasma. It is known that hydrogen plasma bombardment of silicon at 350°C

can produce near surface concentrations[8] of hydrogen of ~ 10^{21} cm^{-3} compared to the melting point solubility[9] of ~ 10^{15} cm^{-3}. This is clear evidence for plasma-induced damage in this region. However, under our conditions (p = 0.1 Torr, excitation at 13.56 MHz), the oxygen ions should have mostly thermal energies. It is known[10] that under these same plasma conditions the atomic diffusion of H is not significantly enhanced when compared with electrolytically injected atomic H,[11] although such an enhancement could be present for oxygen diffusion.

The reduction in effective diffusivity of H at low temperatures by molecule formation and trapping at defect sites is marked (effective diffusivity is about three orders of magnitude lower than expected from high temperature extrapolation)[1] and could mask any apparent enhancement due to point defect phenomena. The recombination of atomic O, by contrast, appears to be much less severe at low temperatures in silicon, if atomic O is the diffusing entity. Oxygen would have less affinity for pairing with dangling or defective bonds (the opposite of atomic H) created by plasma bombardment or already present in the crystal. Thus an enhanced diffusivity might be expected for unbound atomic O compared with atomic H. It has already been suggested that O_2 may be a mobile species[4] in silicon at low temperatures and we cannot rule out AO_2H formation during the sequential O, H plasma treatment or during H_2O plasma exposure.

It has been suggested previously that bound interstitial O may have a much higher (four orders of magnitude) effective diffusivity at the thermal donor formation temperature (450 C) than indicated from extrapolations of the high temperature diffusion data.[4] Stavola, _et al._[12] have observed an anomalously fast diffusion of bound interstitial O at low temperatures (~ 300 C) in samples that have not received a high temperature "soaking"

treatment to disperse O clusters. It is possible that such effects are related to our observation of a rapid diffusion for an oxygen species introduced from a plasma source at near ambient temperature.

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FIGURE CAPTIONS

Fig. 1. Diffusion constant D_O for the mobile oxygen species in p-type silicon as determined using the neutralization of boron acceptors. The effective diffusion constant D_H of free atomic hydrogen as determined in Ref. 1 is shown for comparison.

Fig. 2. Annealing behavior of oxygen bound to boron (AO^-) in silicon. Each curve is for a separate sample exposed first to an O_2 plasma for 40 min at 110°C, heated for 5 min at the temperatures indicated and then exposed to an H_2 plasma for 3 h at 110°C to form the neutral complex AOH.

Fig. 3. Data from Fig. 2 plotted as the integrated fraction of AO^- remaining after annealing. The solid line corresponds to $N/N_O = \exp -[t\nu \exp -(E_D/kT)]$ for $E_D = 1.60$ eV and $\nu = 10^{14} s^{-1}$.

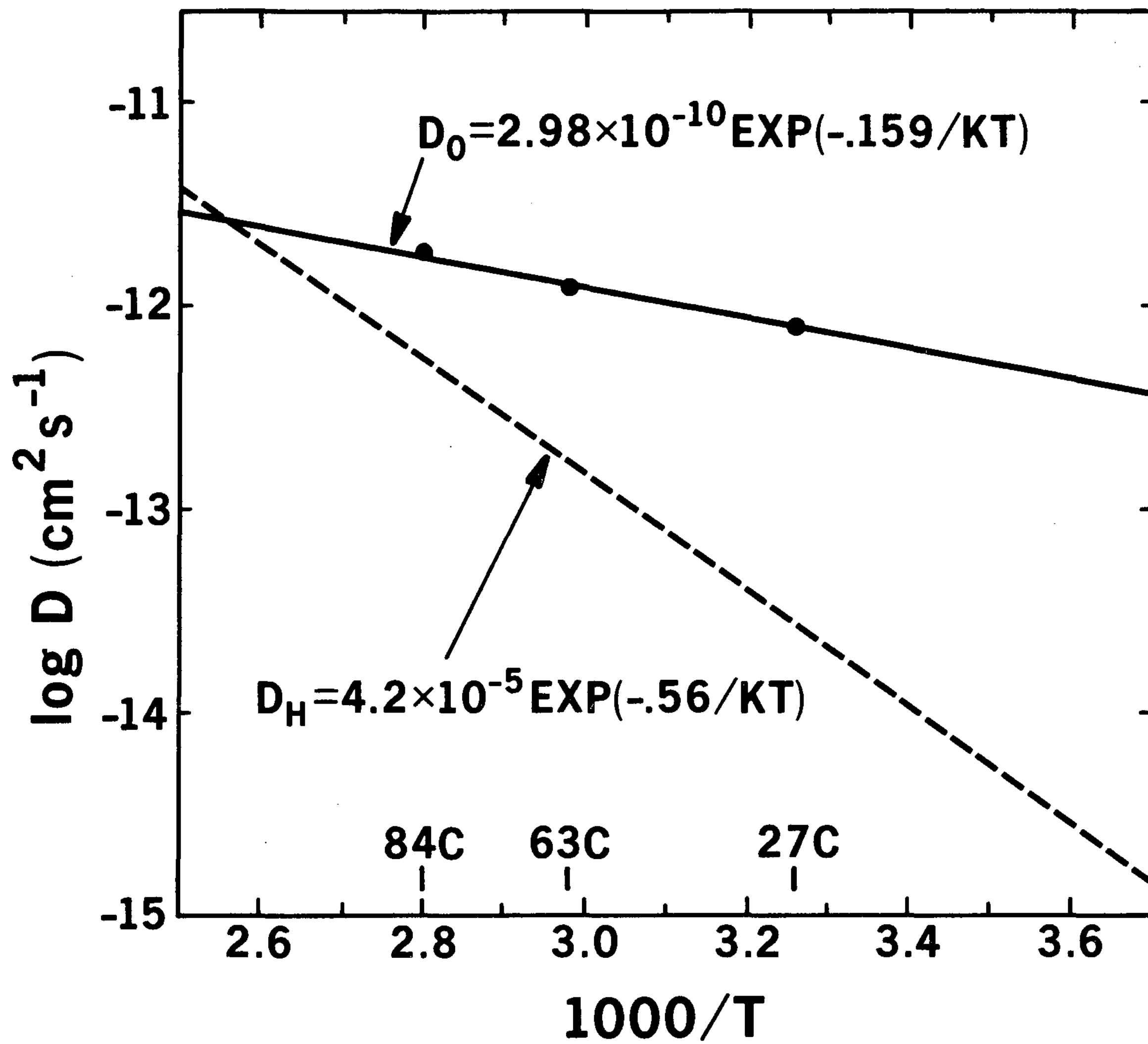

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Figure 1.

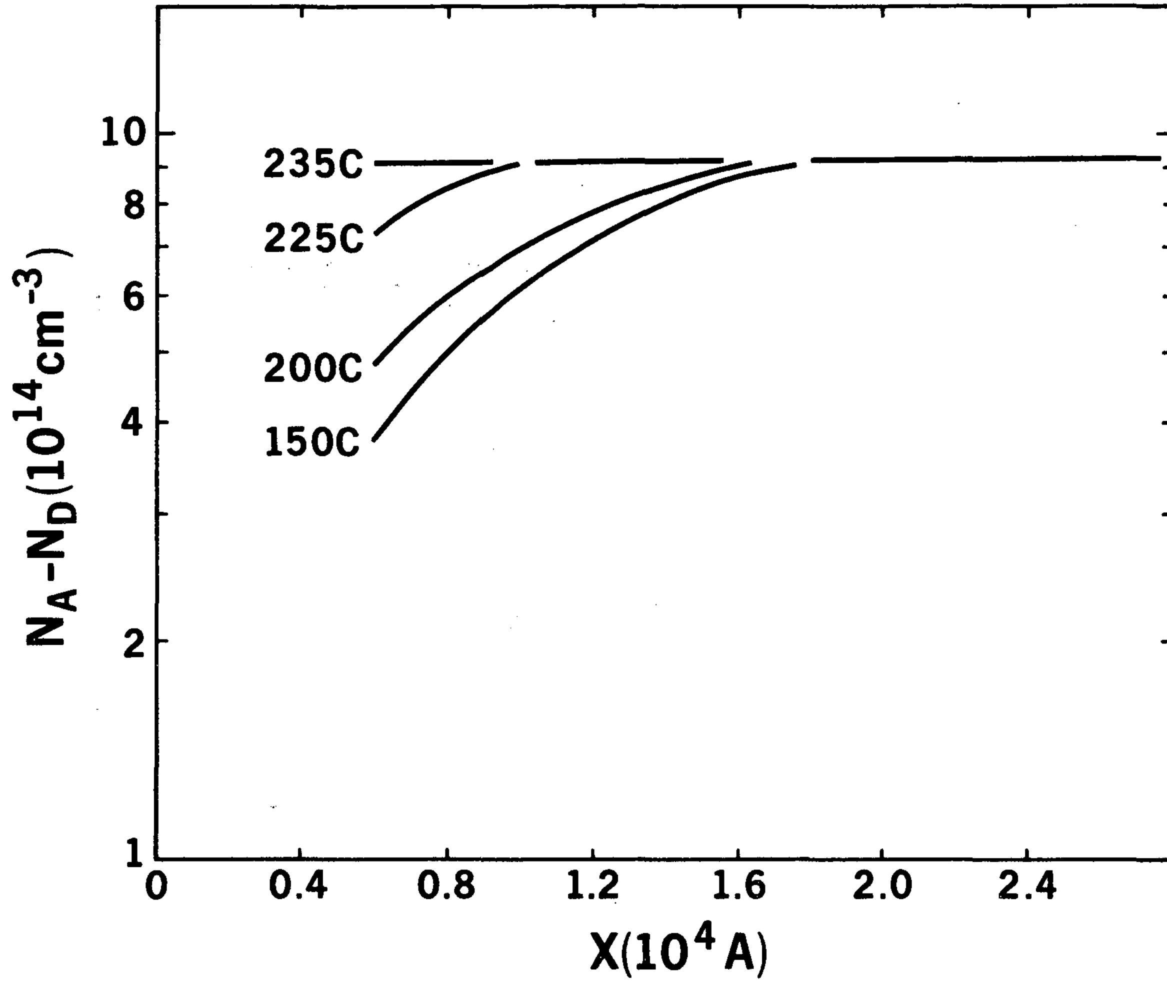

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Figure 2.

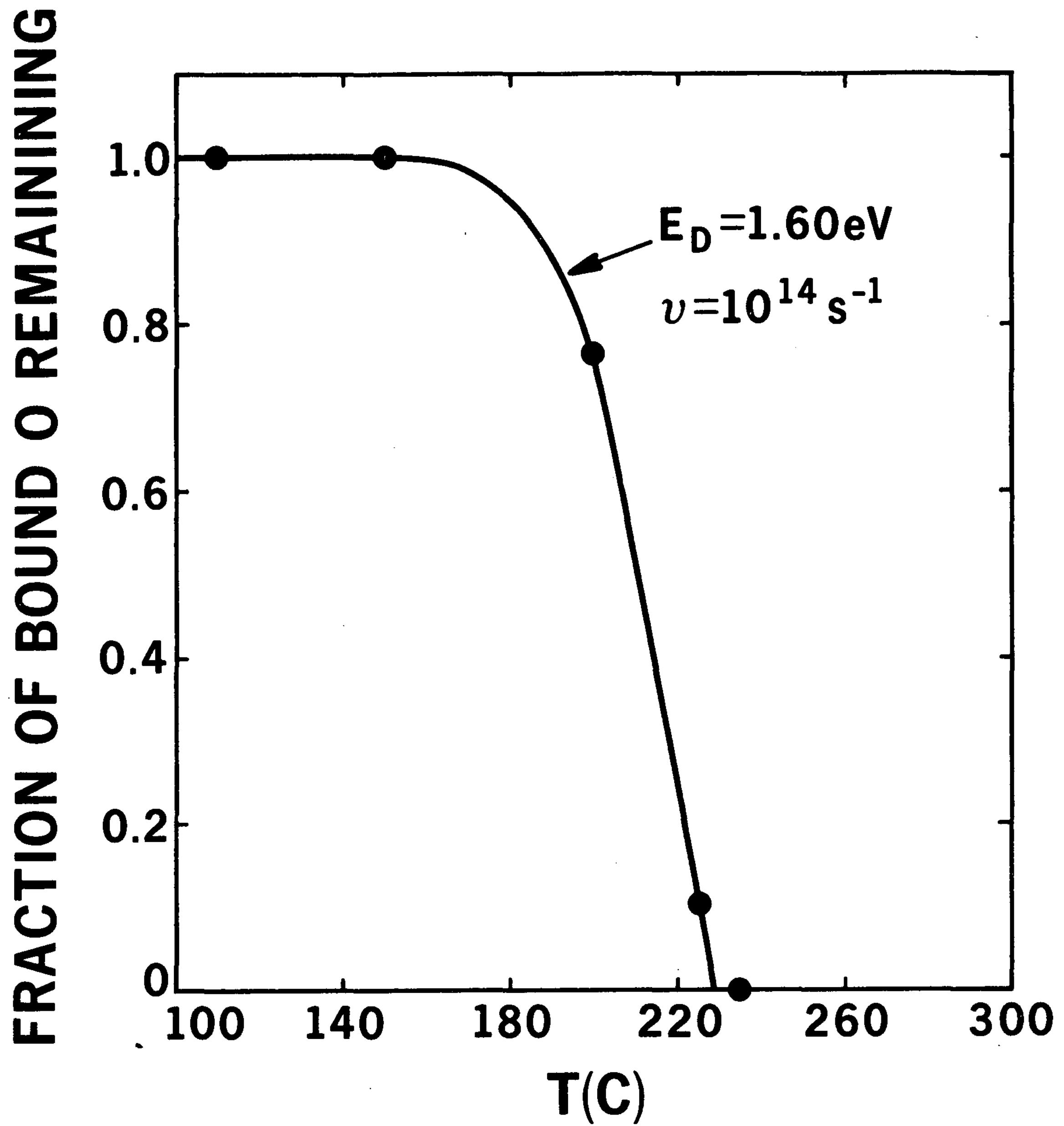

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Figure 3.

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