of the possible errors attending transportation of a group of standard cells to BIPM and return. The estimated value of this uncertainty was set at 0.2 ppm from which we determine $2e/h = 483.593\,84 \pm 0.000\,10$ MHz/μV_{BIPM69}. This result is 0.4 ppm greater than the value obtained by Finnegan, Denenstein, and Langenberg for evaporated film junctions and 0.1 ppm greater than the mean of Petley and Morris for solder-drop junctions. The measurements using Josephson junctions by which voltage is referred to frequency have been made with greater accuracy than can be obtained for the comparison of the various national voltage standards. Further refinements in the Josephson measurements are possible and it is to be expected that the Josephson junction will replace the standard cell as the primary voltage standard for national standards laboratories.

The authors wish to acknowledge the valuable contribution of R. Holmes who carried out the regular comparisons of the divider resistors with the series-parallel set. The cooperation of the Division of Physics in the setting up of the cryogenic apparatus is also gratefully acknowledged.

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EXPERIMENTAL-CONDITION DEPENDENCE OF PHOSPHORUS DIFFUSIVITY IN SILICON

R. N. Ghostagore
Westinghouse Research Laboratories, Pittsburgh, Pennsylvania 15235

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Radiophosphorus diffusion in (111) silicon, under intrinsic conditions from an oxide source in air and from doped silicon sources (epitaxial, polycrystalline, and vapor phase) in a hydrogen atmosphere, has conclusively demonstrated the pronounced effects of both the free surface and the redox reaction on the apparent phosphorus diffusivity in silicon.

In silicon-device technology, phosphorus is diffused into silicon from an oxide source in a controlled oxidizing atmosphere. Consequently, all the diffusion data in the literature for phosphorus into silicon have been obtained by some variation of the same basic experimental technique. The purpose of this Letter is to show that all such data have unsuspectedly included some recently discussed[1,2] surface effects.

Phosphorus-32 in the form of phosphorus trichloride in silicon tetrachloride was used as the basic source in this set of experiments. All the wafers were of float-zoned, low-dislocation-density (~10^3/cm^2), boron-doped (~1×10^{15} cm^{-3}), 15- to 18-mil-thick silicon of (111) orientation and with a mirror finish (by chemical polishing). On the first set of substrates, a 6- to 12-μm-thick P^{32}-doped epitaxial layer of silicon was grown at 1250°C (by the hydrogen reduction of $SiCl_4$) and served as the diffusion source. The surface of this epilayer was covered with a 2000- to 2500-Å-thick layer of amorphous Si_3N_4 (by the reaction of SiH_4 and NH_3 at 800°C) which served as an out-diffusion barrier. On the second set of substrates this P^{32}-doped source layer was deliberately made polycrystalline (at 1050°C). It was also similarly Si_3N_4 covered. Both of these sets of samples were then diffusion annealed and profiled for phosphorus concentration as described earlier.[3]

The next set of diffusion experiments were done in air and in an induction-heated furnace by coating the substrates with a 2- to 3-μm-thick layer of $P_2O_5+SiO_2$. This was accomplished by allowing $P^{32}Cl_3$-doped $SiCl_4$ (in argon carrier gas) to react with moist carbon dioxide (at atmospheric pressure) at 850°C on a quartz-encapsulated graphite susceptor in a rf-heated "silicon epitaxial" reactor. The final set of P^{32} diffusions in silicon were done in a hydrogen atmosphere (in a resistance-heated furnace) with P^{32}-doped powdered silicon (on a quartz boat) as the diffusion source. After diffusion the wafers with the oxide source were etched in HF to remove the

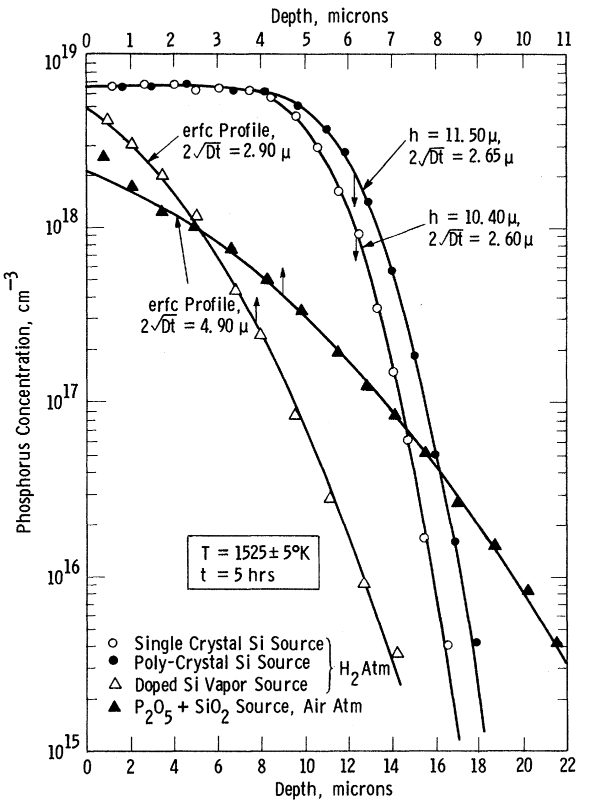

FIG. 1. Phosphorus concentration profiles in (111) silicon obtained by the four different types of diffusion experiments.

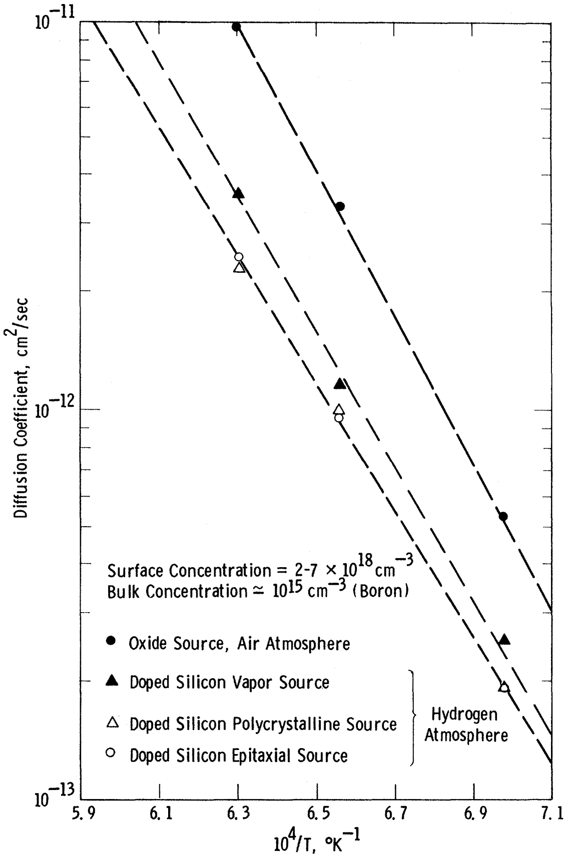

FIG. 2. Phosphorus diffusivities in (111) silicon as a function of temperature under different experimental conditions.

surface oxide. Then, both these diffused samples and those obtained after diffusion from the powdered silicon source were chemically sectioned to obtain phosphorus tracer concentration profiles.[3] The last two types of phosphorus concentration profiles satisfactorily conformed to a complementary-error-function distribution, as expected. Figure 1 illustrates the comparative phosphorus concentration profiles obtained in all four types of diffusion experiments at 1525 ± 5°K. The best-fit theoretical profiles are also shown. Phosphorus diffusion coefficients obtained from these profiles and those at two other temperatures are shown as a function of inverse absolute temperature in Fig. 2.

The phosphorus diffusion coefficients obtained under oxide-source diffusion conditions satisfactorily agree with both Mackintosh[4] and Maekawa[5] (for similar surface and bulk impurity concentrations). However, much lower diffusivities of phosphorus are obtained by the other three types of diffusion couples. The next lower diffusivity values (at a fixed temperature) were exhibited in the case where only the redox reaction at the silicon surface was eliminated by the use of a P^{32}-doped silicon vapor source in hydrogen atmosphere. The lowest diffusivities, however, were obtained where both the free surface and the redox reaction on it were eliminated by the use of epitaxial or polycrystalline P^{32}-doped silicon surface layers (in hydrogen atmosphere) as the diffusion source. The equivalence of the polycrystalline source to the epitaxial source would seem to indicate that at these high temperatures the grain-boundary high-diffusivity paths are not particularly favored by the controlling point defects.

It is now clear that both the free surface and the chemical redox reaction on it enchance the diffusivity of phosphorus in silicon. This in turn is probably related to a nonequilibrium transient vacancy concentration profile near the surface, if the vacancy mechanism of diffusion is assumed. The quantitative effects of a free surface and the surface oxidation of silicon on the vacancy concentration near the surface at any temperature, however, still remain to be delineated in detaill before the phenomena reported here can be properly analyzed and understood.

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OBSERVATION OF LIBRON-LIBRON INTERACTIONS IN SOLID HYDROGEN*

C. F. Coll, III, A. B. Harris, and A. J. Berlinsky
Department of Physics, University of Pennsylvania, Philadelphia, Pennsylvania 19104

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The anharmonic interactions between librational waves in solid hydrogen are found to lead to significant perturbations in the single-libron spectrum. This large anharmonicity is also responsible for two-libron processes whose frequencies and Raman intensities are calculated. Our results for the one- and two-libron spectra are in excellent agreement with, and hence explain, the optical data.

Ever since Dyson's famous paper in 1956 on spin-wave interactions in a ferromagnet,[1] great efforts have been made to observe these interactions. However, since long-wavelength spin waves interact only very weakly, this has been a difficult experimental problem, and only in the last few years has the optical observation[2] of two-magnon states in antiferromagnets[3] shown unequivocally the existence of these interactions. The existence of anharmonicity in phonon systems is also documented,[4] but here the fundamental interactions are less well known and hence many calculations[5] use anharmonic force constants which are not evaluated from a microscopic point of view. In contrast, in solid hydrogen the relevant orientational interactions between molecules are determined from first principles,[6] and hence the associated anharmonic force constants are well known. Furthermore, since these anharmonic interactions are large,[7] the orientational excitations in solid hydrogen constitute a unique many-body system.

The elementary excitations of this system are the small librational motions of the molecules about their equilibrium orientations. In the orientationally ordered phase [which occurs for the pure ($J=1$) solid below about 3°K for H_2 and 4°K for D_2] the fcc crystal consists of four interpenetrating simple-cubic sublattices, each of which consists of molecules oriented along one of the various [111] directions.[8,9] Since there are four molecules per unit cell, each of which can librate in two perpendicular directions, the librational excitation (libron) spectrum has eight branches.[10-14] In this approximation the effects of zero-point phonon motion and phonon-libron interactions are taken into account only insofar as they renormalize the orientational interactions,[15,16] of which the quadrupole-quadrupole interactions scaled by the parameter[10-16] Γ are the most important. From the symmetry of the four-sublattice structure, space group $T_h^{(6)}$, one expects at $k=0$ one twofold degenerate and two threefold degenerate libron energies.

These elementary excitations have been observed directly via Raman scattering of light.[17] However, the interpretation of this spectrum has been unclear for two reasons. First, there were observed five lines in the Raman spectrum instead of three as predicted from theory. Second, the calculated libron energies did not agree very well with any reasonable assignment of the observed lines. Accordingly, a distortion to a lower symmetry structure was suggested.[17] From x-ray work[18] a similar distortion has been suggested for solid N_2. However, the distortion in solid N_2 has not been confirmed by subsequent optical data,[19] and hence its existence is uncertain. For solid hydrogen, a distortion is not a plausible explanation of the spectrum, because it must be supposed to produce rather large splittings in the Raman spectrum. Recently Nakamura[20] has suggested that the extra lines may be due to two-libron processes. However, the mechanism he proposed relied on the zero-point disorder in the orientational system, and consequently the intensity associated with this process was very small.

Here we propose a mechanism for a two-libron absorption which can account for these two extra