SAND--79-0657C
Conf. 791127--8

ION CHANNELING STUDIES OF HYDROGEN LATTICE LOCATION*

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ABSTRACT

The application of ion channeling to study the lattice site location of hydrogen in solids is briefly reviewed. The technique has been applied to both metals and semiconductors and is particularly valuable when combined with ion implantation for the introduction of hydrogen in the study of hydrogen trapping by defects.

The ion channeling effect is an atomic collision phenomenon which was first investigated in the mid 1960's and is relatively well understood today. It occurs when an energetic beam of particles is aligned with crystal rows or planes. Under such conditions, the channeled particles are steered by the lattice rows or planes through a series of correlated coulombic collisions, much like a stone skipping off the surface of water. The channeling technique allows one to determine the position of impurity atoms within the crystal lattice, both for substitutional and interstitial impurities.[1] Localizations of ≈ 0.1-0.2 Å are typically achieved in high symmetry cases. The technique is unlike diffraction techniques which require periodicity of sites or inelastic techniques which give the symmetry of sites, but rather corresponds to a direct imaging technique giving a relative position of the impurity atoms with respect to the position of the lattice rows or planes.

The use of the ion channeling technique to study the lattice location of hydrogen in crystals has provided some of the most discrete and fascinating information on impurity site structures obtained by this technique. Direct determination of the crystallographic site of hydrogen is important since it provides a link between theory and detailed trapping and migration studies. Channeling effect studies of hydrogen have been applied by several groups, both for the case of hydrogen introduced by diffusion in crystals with high hydrogen solubilities such as Nb and

*This work supported by the U. S. Department of Energy, Office of Basic Energy Sciences, under Contract DE-AC04-76-DP00789.

†A Department of Energy Facility.

Pd,[2] and also for hydrogen introduced by ion implantation in crystals with low solubilities such as Al, W, and Si.[3,4]

The use of ion beams to study hydrogen in solids has several distinct advantages.[5] Ion implantation allows the controlled introduction of hydrogen independent of thermodynamic constraints. Thus, hydrogen can be introduced over a wide range of concentrations, from the dilute phase up to very high concentrations above the solid solubility, in a single set of experimental studies. Secondly, the use of energetic beams provides for a sensitive method to detect hydrogen, primarily through ion-induced nuclear reactions or ion scattering or recoil techniques. This allows isotopically selected detection of the hydrogen and also gives the capability to nondestructively determine the absolute hydrogen concentration vs depth profile. Finally, defects are introduced in conjunction with hydrogen implantation and a particularly fruitful area of study is that of hydrogen-defect interactions. Such defect interactions strongly affect the hydrogen mobility, and the understanding of hydrogen transport is quite important to developing a quantitative description of the hydrogen embrittlement process.

In applying the channeling technique to lattice location studies there are several limitations which must be borne in mind. The site of interest must be populated to a significant extent (> 20%). Secondly, a limited number of sites must be populated, preferably two or less, of moderately high symmetry to allow accurate and unambiguous interpretation of the results. Thirdly, defects can be introduced by the analysis beam during channeling measurements and this sometimes sets a practical lower limit to the concentrations which can be studied; typically concentrations ~ 0.1 at.% can easily be investigated. Finally, the channeling technique provides the site of the hydrogen but does not provide information on the local configuration of the surrounding host atoms.

In Fig. 1 the principle of the channeling effect technique for locating impurities is shown schematically. Under channeling the spatial distribution of a beam of particles is strongly modified from a uniform distribution to one which has a high probability density in the center of the channel and a low density at the position of the atoms in the rows or planes. As seen for axial channeling in Fig. 1 this distribution depends on the incident angle of the beam. Thus by monitoring the particle flux density by nuclear reactions or ion scattering a given impurity position in the channel will give rise to a characteristic angular dependence. For example, positions a and b correspond to the projected positions of the tetrahedral interstitial site along the <100> axis in a bcc crystal and the corresponding peaks in the angular yield curve shown below are indicated. This characteristic signature for the impurity which is obtained

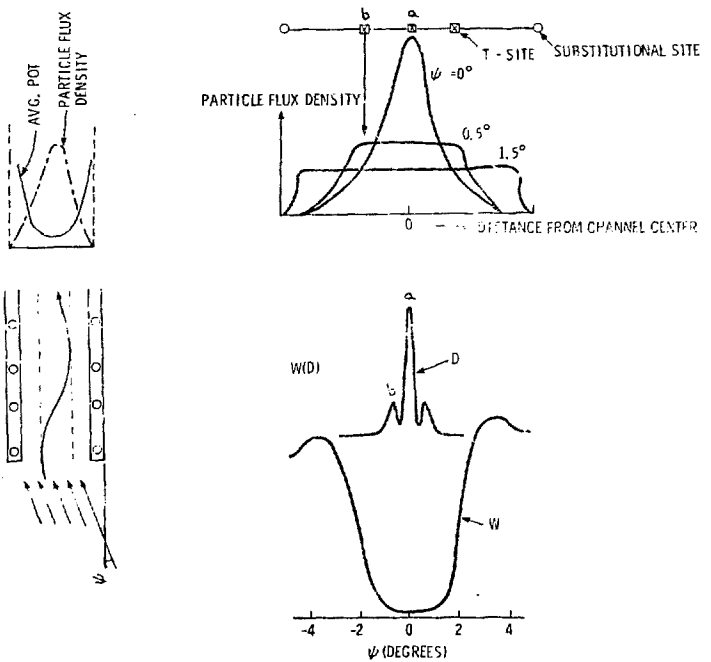

Fig. 1. Schematic of the principle of lattice location by the channeling effect.

simultaneously with that of the host crystal is referred to as the angular distribution and is observed directly in the channeling measurements.

The angular distribution for the case of D implanted into W is illustrated in Fig. 2. The D isotope is detected by the nuclear reaction $D(^3He,p)^4He$ where the high energy emitted protons (≈ 13 MeV) are easily detected with essentially zero background arising from other interactions due to the 0.75 MeV incident ^3He beam. The W signal is obtained from ^3He backscattering from the W lattice atoms. The experimental data is shown

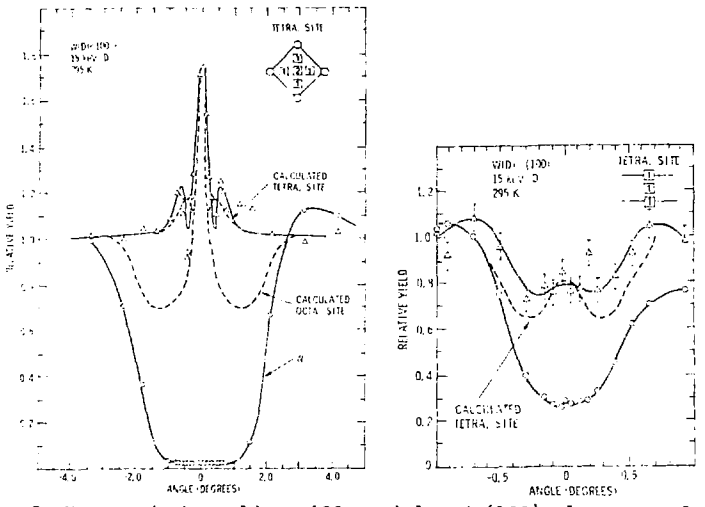

Fig. 2 Measured channeling <100> axial and (100) planar angular distributions for D implanted into W. Dashed lines are calculated distributions and comparison indicates the D occupies the tetrahedral interstitial site.

in Fig. 2 for both the <100> axial and (100) planar directions, along with theoretically calculated distributions (dashed lines) for the hydrogen on the tetrahedral and octahedral interstitial sites. The octahedral site distribution for the case of the (100) planar direction coincides with that for the W crystal lattice. Also shown in the insets are the projected positions for the tetrahedral sites corresponding to these particular channeling directions. As is seen in Fig. 2, relatively good agreement is obtained between calculation and measurement for D occupancy of the tetrahedral interstitial site in W. This site is observed both for implantations at 90 K and also for implantation or anneal temperatures up to ≈ 400 K.[4] Comparison with other experimental studies of hydrogen isotopes in W suggests that D occupies the tetrahedral site both in its untrapped and trapped state and that at room temperature and above the deuterium may be in association with a lattice defect.

A second example is given by studies of D implanted into the other Group VI transition metals Cr and Mo.[6] Results are shown

in Fig. 3 for the <100> axial distributions after low temperature D implantation and subsequent annealing to 300 K. In this case the annealing results in the movement of the D from an appreciable fraction in the tetrahedral interstitial site to a new well-defined position near the octahedral interstitial site. Detailed analysis of the axial and planar data suggests that a single site is occupied with the D displaced from the exact octahedral interstitial site as indicated by I for the case of Cr (displacement distance ≈ 0.3-0.4 Å) and by II in the case of Mo (displacement distance ≈ 0.2 Å). Both calculated and measured distributions are shown for Mo whereas for clarity only the calculated distribution is shown for Cr. The results indicate the D is trapped and suggest trapping by a defect, although D-D interactions cannot be excluded at this time. This site is observed to be stable below stage III and one possible interpretation is that the D may be associated with a lattice vacancy. For example, in the case of site II for Cr the symmetry suggests the possibility of a vacancy in the nearest-neighbor site, corresponding to the top or bottom of the octahedron of lattice atoms shown in Fig. 3. However, the theory of hydrogen-defect interactions in metals is insufficient at this time to provide direct theoretical comparisons to this possible interpretation.

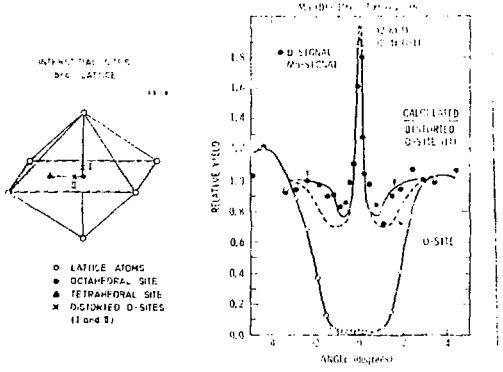

Fig. 3 The <100> angular distributions for D implanted in Mo and Cr (Cr data points not shown for clarity) after anneal to 300 K are shown along with the calculated distributions for the interpreted near-octahedral sites.

In other recent applications the first location studies of hydrogen in a semiconductor have been carried out.[7] This has allowed comparison of the location to be made for a case where chemical trapping should dominate, in contrast to the physical trapping to defects expected for the case of metals. In Fig. 4 the interpreted location of D in Si is compared to several other known interstitial centers in Si determined by electron paramagnetic resonance. The observed site is different than that anticipated to be predominately populated by theoretical calculations, but shows qualitative similarity with other interstitial impurities in Si. The [illegible] is believed to be associated with a lattice defect such as a vacancy or possibly an interstitial Si. One of the advantages of hydrogen studies in a semiconductor over metals is that optical techniques such as infrared absorption can also be used to probe the hydrogen local mode vibrations. Such studies provide information on the surrounding structure and clearly suggest that the H/D is in association with defects in Si.[8]

Recently, channeling effect measurements in combination with detailed detrapping kinetics studies have been applied to the

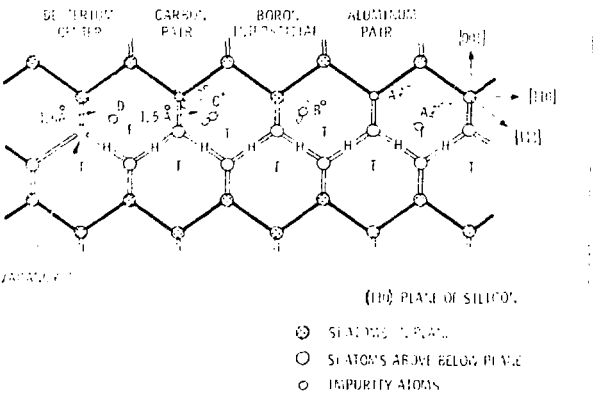

Fig. 4 The (110) plane of Si showing the site for D determined by ion channeling and several other interstitial impurity sites determined by EPR.

case of D implanted in Fe.[9] This has provided detailed information on D in Fe, including the first lattice location measurements. Such work is relevant to H migration in Fe-based systems and to developing improved understanding for a more quantitative description of H embrittlement processes. Further application of the channeling effect technique in the area of H trapping in technologically relevant materials would appear to be a very fruitful direction for such studies.

REFERENCES

1. S. T. Picraux, New Uses of Ion Accelerators, Ed. by J. F. Ziegler (Plenum, NY, 1975) p. 229.
2. H.-D. Carstanjen, Ion Beam Surface Layer Analysis, Vol. 2, Ed. by O. Meyer, G. Linker, and F. Kappeler (Plenum, NY, 1976) p. 497.
3. J. P. Bugeat, A. C. Chami, and E. Ligeon, Physics Letters 58A, 127 (1976).
4. S. T. Picraux, Ion Implantation for Materials Science and Technology, Ed. by J. K. Hirvonen (Academic, NY, 1979).
5. S. T. Picraux, Physics Today 30, No. 10, 42 (1977).
6. S. T. Picraux, Ion Beam Surface Layer Analysis, Vol. 2, Ed. by O. Meyer, G. Linker, and F. Kappeler (Plenum, NY, 1976) p. 527.
7. S. T. Picraux and F. L. Vook, Phys. Rev. B18, 2056 (1978).
8. S. T. Picraux, F. L. Vook, and H. J. Stein, Proc. Int'l. Conf. on Defects and Radiation Effects in Semiconductors (Institute of Physics, London, 1979), in press.
9. S. M. Myers, S. T. Picraux, and R. E. Stoltz, J. Appl. Phys. (to be published).