PHYSICAL REVIEW B VOLUME 26, NUMBER 8 15 OCTOBER 1982

Investigations on the origin of nuclear quadrupole hyperfine parameters of implanted ^{125}Te and ^{129}I in semiconductors

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(Received 29 March 1982)

Recent Mössbauer measurements on ion-implanted ^{125}Te and ^{129}I in silicon and germanium have provided information about the quadrupole interaction in these systems. Using a model for these systems of an impurity close to one member of a divacancy in the semiconductor and a self-consistent-charge extended Hückel procedure involving a cluster of atoms including the impurity atom, we have analyzed the field gradients at the ^{125}Te and ^{129}I nuclei. Our analysis supports the proposed model for these impurity systems and provides Te—Si, Te—Ge, I—Si, and I—Ge bond lengths in these systems of 2.49, 2.54, 2.41, and 2.48 Å, respectively. The relationship of these results to measured bond lengths associated with host and adsorbed atoms at surfaces of semiconductors will be discussed.

I. INTRODUCTION

Numerous efforts have been devoted to the doping of type-IV semiconductors with Te impurities, both by diffusion and ion-implantation techniques. The low solubility of Te in Si and Ge has tended to favor ion implantation as the appropriate doping technique for high dopant concentration, but even in this case the early results were far from satisfactory. Although Rutherford backscattering (RBS) investigations on the location of the implanted Te impurities were started more than a decade ago,[1,2] some decisive progress in the understanding of this system could be made only recently after the introduction of Mössbauer spectroscopy.[3–5] In particular, Mössbauer-effect studies using recoil-less γ-ray transitions in the decay of ^{125}Te^m and ^{129}Te^m isotopes are not completely in agreement with the early channeling results,[1,2] according to which Te implanted in Si at 350 °C and subsequently annealed would predominantly occupy regular substitutional positions. The Mössbauer spectra of ^{125}Te and ^{129}I (daughter isotope of ^{129}Te^m possessing the Mössbauer level) show conclusive evidence for the presence of nuclear quadrupole splittings due to electric field gradients (EFG's) at the nuclei of a majority of the Te dopants, which is not compatible with a lattice site of cubic symmetry, such as a regular substitutional one. Evidence for a noncubic Te surrounding has been independently presented by time-differential perturbed-angular-correlation measurements,[6] which were also based on the detection of nuclear quadrupole interactions.

A few years ago, the quality of Te-implanted samples was dramatically improved by the use of laser-annealing techniques.[7] It is well known that laser annealing possesses superior efficiency for shifting impurities into substitutional locations. Indeed, both RBS (Ref. 8) and Mössbauer experiments[9] agree on the fact that a majority of the Te dopants in Si are found at substititional sites after laser annealing. The situation is less clear for I since Mössbauer measurements performed on ^{129}I in Si after laser annealing exhibit a quadrupole splitting attributed to a trigonal Jahn-Teller distortion of the substitutional I site under certain doping conditions.[10]

In spite of this wealth of experimental information, a consistent interpretation of Mössbauer data in terms of the electronic configuration of Te and I impurities is still not available. The present work is focused on the implanted Te and I centers in silicon and germanium and the nature of the noncubic configuration that leads to the observed large quadru-

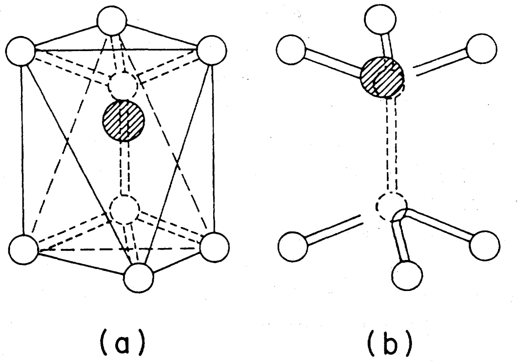

FIG. 1. (a) Model for the location of Te or I implanted in Si or Ge. (b) The $[V_2+\mathrm{O}]$ model (Ref. 14) is shown for comparison.

pole interactions. Dézsi and collaborators have recently proposed a model for this site,[11] which is motivated by the similarity of nuclear quadrupole interaction parameters at the Te site in Te-implanted Ge and in amorphous $\mathrm{Ge}_x\mathrm{Te}_{1-x}$.[12] Neutron-diffraction measurements have suggested that Te is predominantly threefold coordinated with Ge in a-GeTe.[13] The corresponding trigonally coordinated configuration for Te in crystalline Ge or Si has been suggested to be that shown in Fig. 1. In this center the Te atom is associated with a divacancy. Alternately one could describe this center as corresponding to a Te atom close to a substitutional site relaxing towards a neighboring vacancy because of the larger Te—Si or Te—Ge bond length. Additional support for this picture can be found in the fact that oxygen (which is isovalent to Te) when present in Si crystals has often been observed in O-V_2 complexes by electron-paramagnetic-resonance measurements.[14]

Our work is aimed at understanding the origin of the quadrupole interaction in the Mössbauer spectra of ^{125}Te and ^{129}I nuclei implanted in Si and Ge, and in the process also testing the proposed model[11] qualitatively as well as attempting to obtain further quantitative information on the location of the impurity atoms. As proposed in the literature, we shall also use the same model for the I center as in the case of Te impurity. The premise for this assumption is the expectation that the nuclear β decay from ^{129}Te to ^{129}I does not fundamentally disturb the chemical bond between the Mössbauer atom and the host atoms. This similarity of the configurations for the I and Te centers implies that the former carries a positive charge which would make the two centers isoelectronic, which has been supported by empirical arguments involving the isomer-shift data.[11]

A rigorous treatment of the electronic structures of Te and I impurity centers would have to take account[15] of the infinite nature of the solid which is responsible for the band character of the semiconductors. Since we are interested here in examining the configurations of the atoms in the center we have to study a number of such configurations and therefore wanted to utilize a procedure that would not be very time consuming but at least partially take account of the infinite nature of the solid. For this reason, we have carried out cluster calculations using the self-consistent-charge extended Hückel (SCCEH) procedure[16] for our investigation. The extended Hückel procedure has been applied in the past to semiconductor problems both with[17] and without[18] the charge-consistency feature. Our work is similar to that used earlier[19] for the analysis of electric field gradients at ^{125}Te nuclei in Te, Se, and S lattices which compared favorably with experimental values from Mössbauer spectroscopy.

Section II discusses the procedure used in our calculation including the model used for the centers. This is followed by the presentation and discussion of our results in Sec. III. The last section summarizes the main conclusions of our work and further investigations suggested by them.

II. PROCEDURE

We first discuss briefly the procedure we have used for calculations of the electronic wave functions of the impurity centers and the electric field gradients at the impurity nuclei and then the cluster model used for the impurity centers.

A. Procedure of calculation of electronic wave functions and electric field gradient

The SCCEH procedure has been extensively described in the literature.[16] The molecular orbitals of the cluster are expressed as a linear combination of valence atomic orbitals χ_j,

$$\phi_\mu=\sum C_{\mu j}\chi_j \ . \tag{1}$$

In the SCCEH procedure, the matrix elements of the Hamiltonian in the secular equation involved in the variational determination of the molecular-orbital coefficients $C_{\mu j}$ are approximated by the expressions

$$\mathscr{H}_{ii}=I_i^0+q_l(I_i^{\pm}-I_i^0) \tag{2}$$

and

$$\mathscr{H}_{ij}=\tfrac{1}{2}KS_{ij}(\mathscr{H}_{ii}+\mathscr{H}_{jj}) . \quad (3)$$

In Eq. (2) for the diagonal element, I_i^0, I_i^+, and I_i^- are the ionization energies of an electron from the atomic orbital χ_i in the neutral atom, positive, and negative ion, respectively, and q_l the charge on the atom l to which the orbital χ_i belongs. For the off-diagonal element in Eq. (3), S_{ij} is the overlap integral involving the orbitals χ_i and χ_j, and K is an empirical constant, which is taken as 1.75 as in most semiconductor calculations.[17–19] The self-consistency in charge is introduced in the procedure by relating q_l to the molecular-orbital coefficients $C_{\mu j}$ through the Mulliken approximation and carrying out iterations till the input q_l at the beginning of a cycle agrees closely with the output q_l obtained from the $C_{\mu j}$ at the end of the cycle.

From the charge distribution in the cluster, the components of the EFG tensor are computed by taking the expectation values of the operators

$$V_{ij}=\sum_l q_l \frac{3r_{li}r_{lj}-r_l^2\delta_{ij}}{rl^5} + \int \rho(\vec{r})\frac{3r_ir_j-r^2\delta_{ij}}{r^5}d\tau . \quad (4)$$

The first term represents the lattice field gradient due to point charges q_l on the host atoms; it is usually small in a covalent lattice. The second term contains the valence EFG contribution, and its expectation value q_{ij} can be estimated by using the expansion coefficients $C_{\mu p_i}$, belonging to p-type atomic orbital components of the molecular orbitals,

$$q_{ii}=\frac{4}{5}\left\langle\frac{1}{r^3}\right\rangle\sum_\mu \left[C_{\mu p_i}^2-\frac{C_{\mu p_j}^2+C_{\mu p_k}^2}{2}\right]n(\mu) ,$$

$$q_{ij}=\frac{12}{5}\left\langle\frac{1}{r^3}\right\rangle\sum_\mu C_{\mu p_i}C_{\mu p_j}n(\mu), \quad i\neq j . \quad (5)$$

The expectation values $\langle 1/r^3\rangle$ are obtained by using Hartree-Fock wave functions. In our calculation the values $\langle 1/r^3\rangle=11.9335a_0^{-3}$ were used for Te 5p and $\langle 1/r^3\rangle=14.866a_0^{-3}$ for I 5p nonrelativistic orbitals.[20] An enhancement factor of 1.2 was introduced to account for relativistic effects.[21] The available parameters from the experimental side are $V_{zz}=-eq_{zz}$ and in some cases the asymmetry parameter

$$\eta=\frac{V_{xx}-V_{yy}}{V_{zz}} ,$$

assuming that the EFG's are expressed relative to its principal-axis system (PAS) and that $|V_{zz}|\geq|V_{yy}|\geq|V_{xx}|$. Therefore, comparing the calculated EFG tensor with experiment will generally require the former to be diagonalized by switching from the laboratory coordinate system to the PAS.

In all the four systems of interest to us in our present work, we have assumed trigonal symmetry around the impurity nucleus. The asymmetry parameter therefore automatically vanishes and the trigonal axis is the principal axis corresponding to the z direction, that involving the maximum component of the electric field gradient. Mössbauer data[5,11] according to current interpretations also do not provide clear evidence for finite asymmetry parameters for any of the four systems of tellurium and iodine in silicon and germanium.

B. Description of model cluster system

The typical cluster system on which our calculations were carried out is shown in Fig. 1. In this figure, the primary unit involves a divacancy[11] with the tellurium or iodine atom occupying a site close to one of the vacancies. The 16-atom cluster then is composed of the impurity atom, its three nearest-neighbor silicon atoms, the three nearest neighbors of each of the latter, and the three silicon atoms nearest to the vacancy below the impurity atom.

To study the adequacy of this choice, for one of the impurity systems, iodine in silicon, we have studied clusters of size 4, 7, 13, 16, and 43. In the four-atom cluster only the three nearest neighbors of the impurity atom were included, the seven-atom one consisting of in addition the three nearest neighbors of the vacancy below the impurity atom. The 13-atom cluster is related to the four-atom cluster through the inclusion of the nine additional silicon atoms composed of the sets of three nearest silicon neighbors corresponding to the three nearest silicon neighbors of the impurity atom. The 16-atom cluster has already been described and the 43-atom cluster is related to the 16-atom cluster through inclusion of each of the three nearest neighbors of the nine second-nearest silicon neighbors of the impurity atom.

The analysis of the electric field gradients for these five different choices of sizes of clusters led to the following results. The electric field gradients for the four- and seven-atom clusters were not significantly different, indicating the relative unimportance of the influence of the three silicon neighbors next to the vacancy on the electron distribution on the impurity atom. The same conclusions follow from the comparison of the results for 13- and 16-atom clusters. There was, however, significant difference between the electric field gradients for the seven- and 16-atom clusters, indicating the importance of including the second-nearest silicon-atom neighbors of the impurity atom in the upward direction. However, the difference between the 16- and 43-atom clusters was not significant indicating that the third-nearest silicon-atom neighbors on the upward side did not have an important influence on the electric field gradient at the impurity nucleus.

From these considerations, it was felt that as a compromise between practicability and accuracy, a 16-atom cluster would be a satisfactory choice and we have made use of this size for our calculations on the four impurity systems, and the various choices of the position of the impurity atom for each system.

Another consideration for the model systems used was the question of the ends or "surface" of the cluster. In earlier calculations[15] by the extended Hückel procedure for impurity systems in semiconductors, hydrogen atoms were used to terminate the dangling bonds while in SCCEH calculations[19] involving chains of selenium and tellurium atoms, which involved only two terminal atoms, it was found satisfactory to leave these terminal atoms with dangling bonds. However, in our SCCEH work on the present system involving a sizeable number of terminal atoms, the convergence with respect to charges on terminal atoms was not as satisfactory as in the case of tellurium when dangling bonds were present. We therefore tried two other options, one involving termination of the dangling bonds by hydrogen atoms and the other of saturating the dangling bonds with extra electrons adding compensating charges to the pertinent atoms, so that the clusters remained neutral for the tellurium-atom systems and charged for iodine-atom systems. The convergence was better with both these approaches as compared to when dangling bonds were present, the second one of adding extra electrons and compensating charges being somewhat more satisfactory of the two. One does not expect the influence of the nature of the termination of the outermost atoms on the electric field gradient at the impurity site, which is in the internal regions of the cluster, to be of critical importance. This expectation was verified to be correct by carrying out a calculation for iodine impurity with a net positive charge removed from the outer atoms of the cluster. Since there were nine such atoms, this amounted to adding a ninth of a negative charge to each of them. The electric field gradient was found to decrease by only about 0.8% as a result of this change.

III. RESULTS AND DISCUSSION

The electric field gradients V_{zz} are presented in Table I for different displacements z from higher-vacancy positions towards the vacancy below, for all four systems, Te and I in silicon and germanium. The results in Table I indicate that with increase of z, the field gradient V_{zz} decreases as expected from the weakening of the bonds between the impurity atom and the nearest-neighbor silicon and germanium atoms. Further, the dependence of V_{zz} on z is seen to be rather sensitive, justifying the use of fits to experimentally observed V_{zz} to obtain the values of z which determine the positions of the impurity atoms.

In comparing the theoretical values of V_{zz} in Table I with experiment one has in principle to incorporate shielding effects as represented by the equation[22] $V_{zz}^{\text{tot}}=(1-R)V_{zz}$, where R represents the Sternheimer shielding factor.[23] However, R is found to be rather small (about 0.03) from calculations[23] on iodine atom and so one can neglect its effect without much error.

In obtaining the experimental values of V_{zz} for the four systems under analysis from the experimentally measured values of the coupling constants, we have made use of the currently accepted values of 0.31 b (Ref. 24) and −0.68 b (Ref. 25) for the quadrupole moments of ^{125}Te and ^{129}I Mössbauer levels, and 0.55 b (Ref. 26) for the ^{129}I ground state. The values of z and the corresponding bond distances between the impurity and nearest host atoms

TABLE I. Calculated electric field gradients for ^{125}Te and ^{192}I in silicon and germanium. z coordinate indicates the displacement of the impurity atom from the substitutional position along the $\langle 111 \rangle$ axis.

z (Å)	V_{zz} (10^{16} esu/cm^3) TeSi	TeGe	ISi	IGe
0	−2.85	−1.54	−2.13	−1.57
0.1	−2.32	−1.33	−1.56	−1.13
0.2	−1.78	−1.28	−1.06	−0.79
0.3	−1.30	−0.92	−0.83	−0.63
0.4	−0.92	−0.75	−0.62	−0.45

TABLE II. Experimental field gradient V_{zz} (expt), calculated displacement (z), and bond length (R) for Te and I implanted in Si and Ge. Estimated bond lengths R_{cov} obtained from Pauling covalent radii (Ref. 27) are listed for comparison.

System	V_{zz} (expt) (10^{16} esu/cm^3)	z (Å)	R (Å)	R_{cov} (Å)
Te*Si*	−1.16	0.34	2.49	2.49
Te*Ge*	−1.17	0.23	2.54	2.54
I*Si*	−1.28	0.16	2.41	2.45
I*Ge*	−1.24	0.08	2.48	2.50

obtained by comparing the calculated V_{zz} in Table I and experimental values are listed in Table II. Also listed in Table II are the covalent bond lengths expected from the Pauling covalent radii[27] of the corresponding host and impurity atoms. The fact that the interatomic distances derived from the present investigations are close to the covalent bond lengths lends support to the model chosen for the impurity centers. Additionally, our derived interatomic distances are in reasonable agreement with corresponding distances derived from surface extended x-ray-absorption fine structure (EXAFS) measurements[28] on these impurity systems.

Our results and the surface EXAFS results suggest a general conclusion for situations where the impurity atom has the freedom to adjust its location, through for instance the presence of a nearest-neighbor vacancy in the present model, or when it is an adsorbed atom at the surface. The impurity atom in such situations appears to adjust its bond distances with host atoms to be close to covalent bond lengths. Further supporting evidence for this conclusion has also been found recently from x-ray standing-wave measurements[29] for adsorbed bromine atoms on silicon surfaces.

It is difficult to provide a definite confidence limit for the displacements z and bond lengths derived here, because apart from the approximate nature of the SCCEH theory[17] used in the present work we have to take into account the uncertainty on the quadrupole moments of the Mössbauer states,[24,25] both for ^{125}Te and ^{129}I. Moreover, the Mössbauer spectra[5,11] show the existence of a distribution of EFG's whose exact width is rather difficult to estimate. Thus the indicated positions should be considered as an average over a number of slightly different configurations. This is particularly true for the tellurium systems, since the poor resolution of the Mössbauer spectra (due to the large ^{125}Te resonance linewidth) limits the accuracy of the measured EFG. Our intuitive feeling from these considerations is that 25% is a reasonable confidence limit for the displacement parameter z, which corresponds to a confidence limit of 0.03 Å for the nearest-neighbor host-impurity-atom distances. It is noticeable that the position of both impurities are significantly different in Si and Ge. The host-impurity-atom distances in silicon and germanium lattices are smaller for the former for both Te and I impurities, in keeping with the expected trend in view of the larger interatomic distances in pure germanium as compared to pure silicon. Additionally, the Te-host bond lengths turn out to be systematically larger than the corresponding I ones. This result is consistent with the larger Te—Te covalent bond length[27] (2.86 vs 2.66 Å for I—I).

The present investigation does not provide information about the movement of the impurity atom away from the trigonal axis. Clearly, we cannot *a priori* exclude some deviation from axial symmetry, which would result in a nonzero value of the asymmetry parameter η. Unfortunately, experimental data do not give a clear indication for a possible asymmetric location of the impurities. The quadrupole-split ^{125}Te Mössbauer spectrum only contains two resonances, since the nuclear spin is $\frac{3}{2}$, and is therefore unable to provide an independent determination of η in a nonoriented sample. A value of η could in principle be deduced from the ^{129}I spectrum,[30] which contains 16 resonance lines, but the broadening of these lines which display the information on η significantly weakens the sensitivity of the spectrum to the value of the asymmetry parameter. It is hoped that future refinements in channeling and EXAFS techniques will be able to provide a quantitative answer to the question of displacements from the trigonal axis.

IV. CONCLUSIONS

This work constitutes an attempt at understanding of quadrupole interactions of impurity nuclei in semiconductors using electronic wave functions obtained from SCCEH calculations on clusters based on a proposed model[11] for the environment of the impurity. The model has been shown to be reasonable because it is able to explain the observed signs and magnitudes of the experimental nuclear quadrupole coupling constants[11] with choices of the interatomic distances between the impurity atoms and the nearest-neighbor hosts which are rather reasonable in that they are close to the covalent bond distances expected for them. The interatomic distances obtained for the tellurium and iodine systems in the same hosts also follow the trend expected from covalent distances[27] in these systems. In addition to supporting the proposed model, the success of the present investigations lends support to the validity of the SCCEH procedure[16] as a tool for study of hyperfine properties of impurities in semiconductors.

We shall conclude by mentioning future investigations suggested by the present work. On the experimental side, it would be helpful to have more precise measurements of the positions of the impurity atoms by channeling, EXAFS, or other techniques to test the results of the present investigations and also any departures from axial symmetry. On the theoretical side, it would be interesting to extend the present procedure to test the model further by application to related systems such as tellurium in GaAs and other III-V semiconductors, where large EFG's have been observed by Mössbauer spectroscopy.[31] Additionally, it would be desirable in the future to apply more accurate but time-consuming self-consistent procedures[32] to compare with the results of the present investigations.

ACKNOWLEDGMENTS

The authors wish to thank Professor R. Coussement for his continuous interest in this work. They also thank E. van Walle and E. Verbiest for their assistance during the early stages of this work. This work has been partially supported by the National Institute of Health and by the Interuniversitair Instituut voor Kernwetenschappen, Belgium.

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