

Study of the Location of Implanted Fluorine Atoms in Silicon and Germanium through Their Nuclear Quadrupole Interactions*

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Z. Naturforsch. **51a**, 560–564 (1996); received December 12, 1995

Time Differential Perturbed Angular Distribution (TDPAD) measurements of the nuclear quadrupole hyperfine parameters for $^{19}\text{F}^*$ implanted into amorphous, polycrystalline and crystalline silicon and germanium are reported and reviewed. Two signals are observed in the crystalline materials (≈ 35 and 23 MHz in silicon, ≈ 33 and 27 MHz in germanium) while only one is detected in the amorphous and polycrystalline samples (≈ 22 MHz in silicon, ≈ 27 in germanium). Impurity sites in these materials were modeled using a Hartree-Fock cluster procedure. The Intrabond, Antibond, and Substitutional sites in the bulk were studied in both silicon and germanium. The ATOP and Intrabond Surface sites were also studied in silicon and the results extended to germanium. Lattice relaxation effects were incorporated by employing a geometry optimization method to obtain minimum energy configurations for the clusters modelling each site. The electronic wave functions were obtained for each optimized cluster by applying Unrestricted Hartree-Fock theory, and these wave functions were used to calculate the nuclear quadrupole hyperfine parameters at the site of the fluorine nucleus. Comparison of the theoretical hyperfine parameters to the experimental values indicates that $^{19}\text{F}^*$ located in the Intrabond and Intrabond surface sites could readily explain the higher frequency signal that has been observed. $^{19}\text{F}^*$ in the Antibond and the surface ATOP sites yield hyperfine parameters consistent with the low frequency signal observed in the crystalline materials and the single signal observed in the amorphous (or polycrystalline) materials. Examination of these two sites, in view of other available experimental evidence including the temperature dependence of the TDPAD signals, leads to the conclusion that the lower frequency signal is due to $^{19}\text{F}^*$ implants which have come to rest at the site of dangling bonds in the bulk. These dangling bonds are created as a result of damage generated in the individual collision cascades during the implantation process.

Key words: Semiconductors, Impurities, Electronic structure, Hartree-Fock, Electric field gradient.

Introduction

Fluorine impurities are introduced into polycrystalline and single crystal semiconductors during material processing for device applications by implantation and other methods. Time Differential Perturbed Angular Distribution (TDPAD) experiments make it possible to study the environment of implanted fluorine nuclei through the effect of local environment on the nuclear quadrupole interactions at the site of the $^{19}\text{F}^*$ nuclei. $^{19}\text{F}^*$ -TDPAD experiments on single crystal silicon and germanium reveal two sites for implanted fluorine. We used a cluster procedure to

model potential locations for fluorine in the “diamond-like” lattice and to predict the nuclear quadrupole parameters for fluorine at each site.

In the next section, we report and review the results of TDPAD experiments. We then outline the cluster procedure, present the results of our calculations, and finally compare the theoretical results to experimental observations.

Results of TDPAD Experiments

$^{19}\text{F}^*$ -TDPAD experiments were performed on single crystal (c:Si) and polycrystalline (a:Si) silicon samples. “Sandwich” targets were used for the polycrystalline samples. The main sample (Ge, Si) was deposited by vapor deposition on to a thick carbon layer which served as carrier, and was followed by a thin

* Presented at the XIIIth International Symposium on Nuclear Quadrupole Interactions, Providence, Rhode Island, USA, July 23–28, 1995.

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layer of vapor-deposited CaF_2 . In the single crystal targets, the CaF_2 layer was vapor-deposited directly onto the samples. $^{19}\text{F}^*$ nuclei were recoil implanted from the CaF_2 layer into the sample by means of an incident proton beam. The kinetic energy of the pulsed proton beam (2.8 MeV) was chosen to avoid disturbance of the lifetime spectra by superposition of signals from parasitic nuclear reactions due to proton irradiation.

The quadrupole coupling constants, e^2qQ observed for $^{19}\text{F}^*$ in all target materials are presented in Table 1. In all cases the asymmetry parameter, η , was found to be zero, indicating axial symmetry about the principal axis of the efg . Two values of e^2qQ were observed in both c:Si and c:Ge, while only the lower frequency fraction was detected in each of the polycrystalline samples.

Earlier $^{19}\text{F}^*$ -TDPAD measurements [1, 2] performed on c:Si, a:Si and c:Ge samples are also reported in Table 1. These results are in good agreement with those reported here. The higher frequency signals in c-Si and c-Ge were found to be consistent with principal axes of the efg oriented along the $\langle 111 \rangle$ crystal direction while the lower frequency signals were indicative of randomly oriented principal axes. In the amorphous samples the principal axes were randomly oriented, as expected.

When the effect of target temperature on the TDPAD signals was studied [1, 2] it was found that the fraction of $^{19}\text{F}^*$ nuclei occupying high frequency sites in c:Si and c:Ge increased steadily as the target temperature was increased to 900 K. At the same time there was a steady decrease in the fraction occupying the lower frequency sites. In a:Si and a:Ge, site populations were not affected significantly by changes in the target temperature.

Theoretical Procedure

Three potential locations for fluorine in silicon and germanium were studied: Intrabond (IB), Antibond (AB) and Substitutional (S) positions (Figure 1). The study of surface locations is not reported since the fraction of probes with occupied surface sites would not be sufficient to explain the observed signals. Clusters of neighboring atoms were configured to model each site, and dangling bonds at the cluster surfaces were terminated with hydrogen atoms. The effects on the local geometry due to the presence of the impurity

atom, referred to as lattice relaxation, were studied using the Fletcher-Powell method [3] to obtain a minimum energy configuration for the cluster as the location of the fluorine atom, and various groups of neighboring atoms were varied. Variations in geometry were constrained to insure an axially symmetric field gradient at the site of the fluorine nucleus in keeping with the zero asymmetry parameter associated with all observed signals. At each stage in the relaxations the total cluster energies were calculated using Hartree-Fock theory with the STO-3G [4] minimal basis set.

Table 1. Nuclear Quadrupole Coupling Constants for $^{19}\text{F}^*$ in Silicon and Germanium by TDPAD Measurements.

Target	Structure	e^2qQ_1 (MHz)	e^2qQ_2 (MHz)
Silicon	s	35.0	22.6
	p	—	21.07
	s ^a	35.9	23.1
	a ^a	—	23.0
Germanium	s	32.8	26.8
	p	—	27.3
	s ^a	33.4	27.3

^a Measurements by Bonde Nielsen *et al.* [1, 2].

s = Single crystal, p = polycrystalline, a = amorphous, nm = not measured.

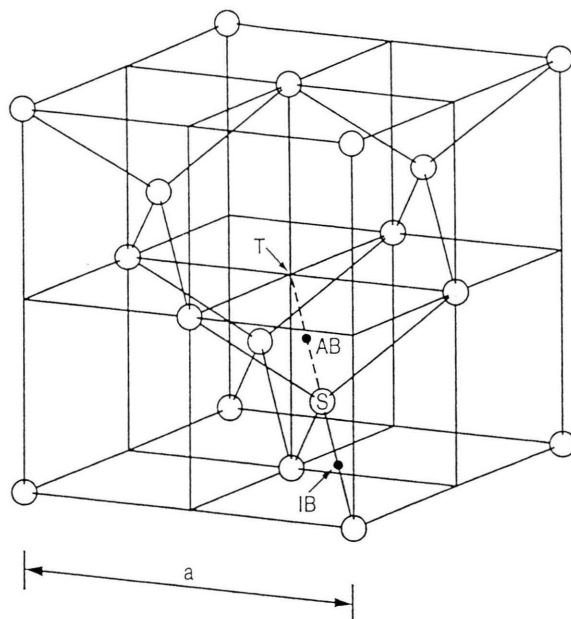


Fig. 1. Location of the Intrabond (IB), Antibond (AB), Substitutional (S), and the Tetrahedral Interstitial (T) sites in silicon and germanium.

The optimized clusters represent the most likely configuration for fluorine and the surrounding lattice in that site. The value of e^2qQ was calculated at the site of the fluorine nucleus in each optimized cluster, using a Hartree-Fock wave function and the 3-21G basis set augmented with polarization functions. All calculations were implemented using the Gaussian [6, 7] series of programs.

Results of Cluster Calculations

The 27 atom cluster, $\text{Si}_8\text{H}_{18}^{19}\text{F}^*$, (Fig. 2) was used in our work to model the IB site in silicon. The two nearest neighbor silicon atoms and the fluorine atom were permitted to relax independently along the $\langle 111 \rangle$ bonding axis. The three atoms in each of the two groups referred to as the Si_i and the Si_j were constrained to vary symmetrically with respect to the $\langle 111 \rangle$ axis in order to preserve the axial symmetry. This was necessary to insure a zero value for η as observed by experiment. The Si_i and the Si_j in the resulting minimum energy cluster were displaced slightly outward while Si_1 and Si_2 were displaced outward by 0.46 Å and 0.58 Å, respectively. The final optimized $\text{Si}_1\text{-F}$ and $\text{Si}_2\text{-F}$ distances were 1.68 Å and 1.71 Å, respectively. The value of e^2qQ obtained was 35.7 MHz.

In an AB location, fluorine lies along the $\langle 111 \rangle$ direction between a silicon atom and the tetrahedral (T) interstitial position where it would be equidistant from that silicon atom, Si_A , and three others, Si_K , Si_L , and Si_M (Figure 1). The 30 atom cluster, $\text{Si}_{11}\text{H}_{18}^{19}\text{F}^*$, (Fig. 3) was used to model the AB site. The fluorine atom and Si_A were allowed to vary independently along the $\langle 111 \rangle$ direction while the three next nearest neighbors, Si_K , Si_L and Si_M , were varied symmetrically with respect to the $\langle 111 \rangle$ axis to preserve the axial symmetry. In the optimized cluster, atoms Si_K , Si_L , and Si_M were displaced slightly outward from the T-site and Si_A was displaced 0.44 Å towards the T-site. Fluorine was located 0.2 Å outside the T-site toward Si_A with a final $\text{Si}_A\text{-F}$ distance of 1.71 Å. The value obtained for e^2qQ was 25.3 MHz.

In a Substitutional location, the fluorine impurity is located near a vacancy in the lattice. In the 26 atom cluster, $\text{Si}_7\text{H}_{18}^{19}\text{F}^*$, used to study this site, the fluorine impurity was placed along the $\langle 111 \rangle$ axis between the vacancy and one of the neighboring silicon atoms. Analysis of the electronic structure of this

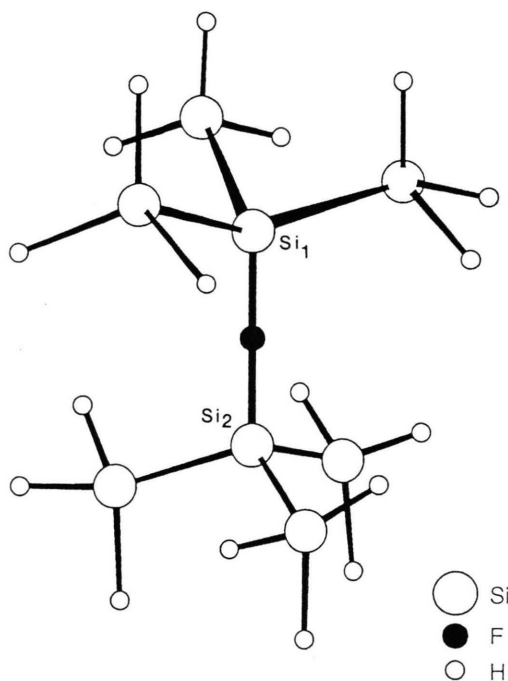


Fig. 2. The 27 atom cluster, $\text{Si}_8\text{H}_{18}\text{F}$, used to model the Intrabond (IB) site.

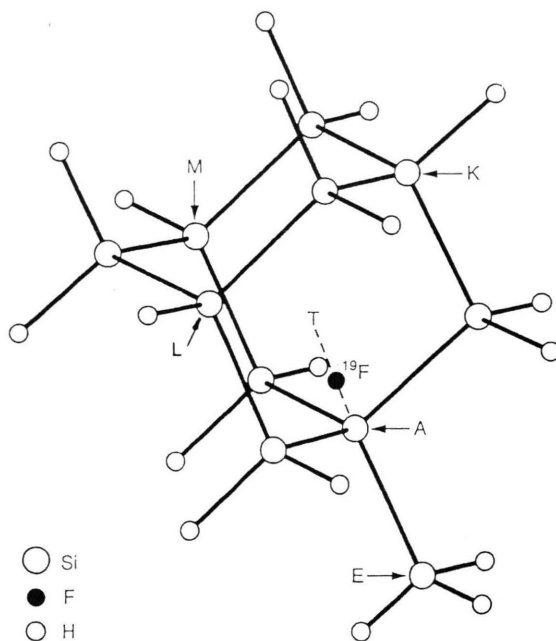


Fig. 3. The 30 atom cluster, $\text{Si}_{11}\text{H}_{18}\text{F}$, used to model the Antibond (AB) site.

cluster indicated that the highest occupied state would be doubly degenerate but only singly occupied. In such a situation, a spontaneous Jahn-Teller distortion [8] would occur to lower the symmetry and remove the spatial degeneracy. Such a state would not be consistent with the zero asymmetry parameter observed experimentally at both sites. Study of the singly and doubly charged versions of this cluster, $(\text{Si}_7\text{H}_{18}^{19}\text{F}^*)^{+1}$ or $(\text{Si}_7\text{H}_{18}^{19}\text{F}^*)^{+2}$, which do not exhibit the spatial degeneracy, yielded values of e^2qQ significantly lower than either of the observed values.

The study of fluorine in the IB, AB and S locations in germanium were performed in a similar manner. The clusters, $\text{Ge}_8\text{H}_{18}\text{F}$ and $\text{Ge}_{11}\text{H}_{18}\text{F}$, were used to study lattice relaxation effects in the IB and AB locations, respectively. In both optimized clusters, the relaxation effects were qualitatively similar to those found in the corresponding silicon clusters. The final optimized Ge-F distances between fluorine and Ge_1 and Ge_2 in the IB location were 1.73 Å and 1.97 Å, respectively. The value of e^2qQ obtained was 33.3 MHz. In the AB region, the nearest neighbor Ge-F distance was found to be 1.77 Å, and e^2qQ was 29.5 MHz. With fluorine in the Substitutional location in germanium, as in silicon, we found that a Jahn-Teller distortion must occur leading to a non-zero asymmetry parameter which is not consistent with the experimental findings.

Discussion and Conclusions

The theoretical values of e^2qQ together with nearest neighbor Si-F and Ge-F distances for the optimized clusters representing the IB and AB sites in silicon and germanium are summarized in Table 2.

Table 2. Theoretical Quadrupole Coupling Constants, e^2qQ , for $^{19}\text{F}^*$ in Silicon and Germanium.

Material	Site	Nearest Neighbor Si-F Distance in Optimized Cluster	e^2qQ 3-21 G ⁺ (MHz)
Silicon	Intrabond (IB)	Si ₁ -F 1.68 Å	35.7
		Si ₂ -F 1.71 Å	
	Antibond (AB)	1.71 Å	25.3
Germanium	Surface ATOP	1.67 Å	27.5
	Intrabond (IB)	Ge ₁ -F 1.73 Å	33.3
		Ge ₂ -F 1.97 Å	
	Antibond (AB)	1.77 Å	29.5

These values can be compared to the observed values of e^2qQ for the single bonds in SiF_4 and GeF_4 of 23.5 and 35 MHz, respectively, and to the Si-F and Ge-F bond lengths of 1.59 Å in SiH_3F and 1.74 Å in GeH_3F , respectively.

In both materials the theoretical values of e^2qQ for fluorine in the IB location are close to the higher frequency observed values. The expected value of zero for η and the expected orientation of the principal axes of the efg along the $\langle 111 \rangle$ direction are also consistent with the observed signals. Thus we predict that $^{19}\text{F}^*$ in IB sites is responsible for these signals.

In silicon, the values of the Si-F distances for the two nearest neighbor silicon atoms are quite similar and are somewhat larger than an Si-F bond length. In addition, e^2qQ is not close to the value typically associated with an Si-F bond. These findings point to an Si-F-Si bridge-like structure, and such a structure has been predicted to be the source of an observed peak in the infrared spectrum of as-implanted samples of fluorine-implanted silicon. In germanium, similar comparisons indicate that in contrast to the situation in silicon, a single bond is formed between fluorine and one of its nearest neighbors.

The theoretical values obtained for e^2qQ in the AB location in both materials are close to the lower frequency observed values. However, fluorine nuclei located in AB locations would be expected to give rise to a signal consistent with a fixed orientation for the principal axis of the efg along the $\langle 111 \rangle$ direction. This is in conflict with the observation that the axes are randomly oriented. Also, there is evidence from supercell calculations [9] that the most stable form for fluorine in the AB location is the negatively charged F^- which moves into the T site where the efg is zero, in which case the AB site would be invisible to TDPAD.

The lower frequency TDPAD signals observed in the single crystal materials are similar to the single signals observed in the polycrystalline and amorphous materials where it is expected that fluorine saturates dangling bonds. This led us to consider the possibility that fluorine may be saturating dangling bonds in the crystalline materials. The "surface" (ATOP) cluster (Fig. 4), $\text{Si}_9\text{H}_{15}\text{F}_3$, was constructed to study this possibility. Relaxation of the three fluorine atoms and each neighboring silicon atom resulted in a final Si-F distance of 1.67 Å and an e^2qQ of 27.5 MHz. This value is close to the observed value associated with the lower frequency TDPAD signal in

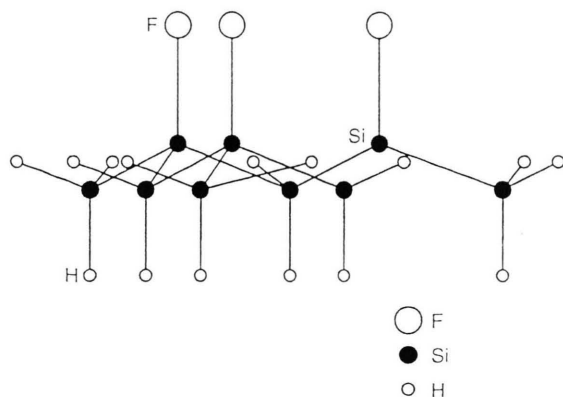


Fig. 4. The 27 atom cluster, $\text{Si}_9\text{H}_{15}\text{F}_3$, used to model the surface ATOP site.

silicon. Since there would not be a sufficient number of dangling bonds pre-existing in the materials, they must be formed during the collision cascade associated with the implantation process. The damage inherent in these regions would then explain the fact that the principal axes of the *efg* are randomly distributed. Finally, this interpretation would explain the temperature dependence of the fractional site populations. As the target temperature is increased, concurrent annealing of the cascade damage will increase and fewer probes will come in contact with dangling bonds, decreasing the fractional population of the lower frequency sites. Since the availability of IB sites would not be expected to depend on temperature, some portion of these probes would come to rest instead in IB sites, thus increasing the population of the higher frequency sites.

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