

Measurements of branching ratios of fragment states or of fragment kinetic energies provide further useful information in addition to that contained in the photodissociation spectra. Similarly, more detailed information can be obtained from photofragment angular distribution and the alignment and orientation of the fragment electronic states [1,13]. Finally, resonant two-photon photodissociation [2] can provide more details by selecting specific intermediate states and by yielding more structure in the angular distribution and alignment of the fragments. In conclusion, more detailed experiments along with multichannel calculations should lead to a better understanding of the dynamics of such complex systems. Our calculations for CH^+ provide the gratifying expectation that the spectra are "just" those anticipated of highly perturbed systems where normal electronic selection rules are largely relaxed.

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AB INITIO CALCULATIONS ON $(\text{SiH}_3)_2\text{F}^+$: STABILITY IN THE GAS PHASE AND MODEL FOR BRIDGING FLUORINE ATOM IN ION-IMPLANTED AMORPHOUS SILICON

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Ab initio calculations have been performed on model molecular clusters simulating bridging fluorine configurations in fluorinated amorphous silicon. Optimized geometries, total energies and vibrational frequencies have been computed for $(\text{SiH}_3)_2\text{F}^+$ clusters with the terminal SiH_3 groups eclipsed or staggered. The stable minimum on the potential energy surface corresponds to a linear, but very flexible, Si-F-Si bridging configuration. $(\text{SiH}_3)_2\text{F}^+$ appears to be stable with respect to unimolecular decomposition. The calculated vibrational frequencies include a strongly infrared-active antisymmetric stretch mode at 740 cm^{-1} , similar to the metastable "B band" experimentally observed at 750 cm^{-1} in the ion-implanted samples. These results are compared with calculated geometries and vibrational frequencies of SiH_3F , SiH_2F^+ , SiH_2F^+ and $\text{Si}_2\text{H}_5\text{F}$.

1. Introduction

Elemental amorphous silicon (a-Si) has a very high density of defects which introduce localized states in its band gap, and cause it to become unsuitable for use as a semiconductor [1]. To overcome this difficulty, Si has been alloyed with H [2], and with H and F [3]. The a-Si:H:F alloys have very interesting optical and electrical properties [4]. It is therefore of great importance to understand the structure and bonding in these alloys at a microscopic atomic level.

It has been pointed out [5-7] that H and F, which have low coordination numbers, can both act as structural bridging and cross-linking elements and as dangling bond terminators, and in addition, decrease the strain energy of the tetrahedral network by re-

ducing its average coordination number. As a result, semiconducting materials of much lower intrinsic defect density and higher quality are obtained. The term "superhalogen" has been used for F, due to its extreme electronegativity, specificity, reactivity and small size, which enable it both to form different types of local bonding configurations, and to penetrate voids in the structures that are too small for the other atoms to enter [5-7].

Recent work on ion implantation of both crystalline and a-Si with polyatomic fluorine-carrying ions, has yielded fluorinated materials where some of the F atoms occupy a type of site different from those previously observed [8]. This work involved implantation of the ions F^+ and XF_n^+ ($\text{X} = \text{B}, \text{Si}, \text{P}, \text{Ge}$; $n = 1, 2$ or 3) into c-Si or a-Si, and measurement of the infrared (IR) and the Raman spectra of the resulting materials. For example, for F^+ and SiF_n^+ implants [8], the three strongest bands in the IR spectra that are attributable to Si-F bonding are at 750 cm^{-1} (B band), 830 cm^{-1} (C band), and 1015

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Table 1
Total energies^{a)}

Structure	Method		
	HF/3-21G	HF/6-31G*	MP3/6-31G**
SiH ₃ F	-388.07406	-390.14840	-390.43723
Si ₂ H ₅ F	-676.62517	-680.22584	-680.62347
SiH ₂ F ⁺	-387.17450	-389.24402	-389.50350
SiH ₃ F ⁺	-387.67568	-389.70171	-390.00662
H ₃ Si-F-SiH ₃ ⁺ (eclipsed)	-676.97563	-680.54930	-680.94557
(staggered)	-676.97553	-	-

^{a)} In au: 1 au = 627.51 kcal/mol.

cm⁻¹ (G band). The B band shows the highest intensity for F⁺ implants, decreasing in intensity in SiF_n⁺ as *n* increases. The B band is also favored over the C and the G bands by lower fluxes of fluorine.

Furthermore, the B band is completely absent in sputtered and glow-discharge a-Si:F films, where the plasma producing the films is unlikely to contain appreciable concentrations of intermediates with a

Table 2
Molecular geometries^{a)}

Structure	Symmetry	Parameter	HF/3-21G	HF/6-31G*
			(optimized)	(optimized)
SiH ₃ F ^{b)}	C _{3v}	R(SiF)	1.635	1.594
		R(SiH)	1.478	1.475
		θ(HSiF)	109.2	108.4
Si ₂ H ₅ F ^{c)}	C _s	R(SiF)	1.644	1.603
		R(Si ₁ H)	1.481	1.474
		θ(SiSiF)	111.2	110.0
		θ(HSiF)	108.5	108.0
SiH ₂ F ⁺	C _{2v}	R(SiF)	1.589	1.535
		R(SiH)	1.453	1.449
		θ(HSiH)	129.4	127.2
SiH ₃ F ⁺	C _s	R(SiF)	1.591	1.538
		R(SiH ₁)	2.529	2.446
		R(SiH ₂ /H ₃)	1.452	1.448
		θ(H ₁ SiF)	96.9	94.7
		θ(H ₂ SiH ₃)	129.2	126.8
(SiH ₃) ₂ F ⁺ (eclipsed)	D _{3h}	R(SiF)	1.767	1.779
		R(SiH)	1.463	1.454
		θ(HSiF)	101.9	101.0
		θ(HSiF)	101.9	101.0
(SiH ₃) ₂ F ⁺ (staggered)	D _{3d}	R(SiF)	1.767	-
		R(SiH)	1.463	-
		θ(HSiF)	101.9	-

^{a)} Bond lengths *R* in Å, bond angles *θ* in deg.

^{b)} Experimental geometry quoted in the JANAF tables [19]: R(SiF) = 1.593, R(SiH) = 1.486, θ(HSiF) = 108.4.

^{c)} Only those geometrical parameters describing the SiH₂F⁺ end of Si₂H₅F are listed.

partial positive charge on F. Finally, at annealing temperatures of *T* ≥ 500°C, the B band anneals out, being replaced by higher intensities of the C and the G bands.

Azarbayejani, Tsu and Lucovsky [8] interpret the metastable B band at 750 cm⁻¹ as arising from metastable bridging F configurations such as Si-F*-Si. This interpretation, which explains the observed phenomena, is also supported by force field considerations [9].

We have undertaken a series of ab initio calculations on small model molecular clusters to simulate various bonding configurations in ion-implanted amorphous silicon alloys. The local environment of the atoms in a solid is simulated by a small finite cluster of atoms, with H atoms used to saturate the remaining valences, as would occur in the solid. Such calculations are among the standard techniques for modeling the properties of solids [10].

formed with the GAUSSIAN 82 system of programs [11], using split valence (3-21G) and split valence plus polarization (6-31G* and 6-31G**) basis sets [12]. All geometrical parameters were optimized with analytical gradient methods [13] at the Hartree-Fock level using the 3-21G and 6-31G* basis sets (HF/3-21G and HF/6-31G*). Theoretical harmonic vibrational frequencies were obtained from analytical second derivatives [14] calculated at the HF/3-21G level. Electron correlation energies were estimated by third-order Møller-Plesset perturbation theory [15] with the 6-31G** basis set (MP3/6-31G**) at the HF/6-31G* optimized geometry. The MP3/6-31G** level of theory underestimates the Si-F bond energy by about 5 kcal/mol, and overestimates the Si-H bond energy by about 3 kcal/mol [16]. The calculated total energies are listed in table 1, geometries in table 2, and vibrational frequencies in table 3.

3. Results and discussion

The implantation of F⁺ ions in amorphous silicon can lead to several bonding situations. For di- and tri-

2. Theoretical methods

Ab initio molecular orbital calculations were per-

Table 3
Harmonic vibrational frequencies (in cm⁻¹)^{a)}

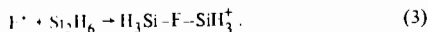
SiH ₃ F	Si ₂ H ₅ F	SiH ₂ F ⁺	SiH ₃ F ⁺	(SiH ₃) ₂ F ⁺ (eclipsed)	(SiH ₃) ₂ F ⁺ (staggered)
800'(728') e	106 a''	763 b ₂	192 a'	16 a ₁ '	34i a _{1u}
943(875) a ₁	164 a'	843 b ₁	307 a''	110 e'	110 e _u
990'(961') e	390 a'	1012 a ₁	390 a'	423 a ₁ '	423 a _{1g}
1132(991) a ₁	406 a'	1093 a ₁	761 a''	694 e''	699 e _g
2338'(2209') e	568 a'	2470 a ₁	847 a'	740 a ₂ '	740 a _{2u}
2352(2206) a ₁	665 a''	2539 b ₂	1007 a'	744 e'	740 c _u
	829 a''		1087 a'	979 e''	983 e _g
	911 a'		2474 a''	991 e'	987 c _u
	925 a'		2541 a''	1014 a ₂ '	1014 a _{2u}
	986 a'			1045 a ₁ '	1046 a _{1g}
	995 a''			2407 a ₂ '	2407 a _{2u}
	996 a'			2410 a ₁ '	2410 a _{1g}
	1046 a'			2441 e''	2441 e _g
	2279 a'			2444 e'	2444 c _u
	2290 a'				
	2294 a''				
	2324 a''				
	2329 a'				

^{a)} Theoretical harmonic frequencies were computed at the HF/3-21G level; experimental anharmonic frequencies are listed in parentheses. The symmetry type of each vibrational mode is indicated after the frequency.

coordinate silicon, F^+ can add to the vacant site, as modeled by the gas phase reactions



For tetra-coordinated silicon, F^+ can insert into a Si-Si bond:



The structures and vibrational frequencies of the gas phase ions are discussed in the next two sections.

These ions can react further, either in unimolecular decompositions, or in bimolecular reactions simulating charge migration and geometry reorganization in the solid. The energetics of these reactions and their implications for the solid are discussed in the last section.

3.1. Geometries

The structures of SiH_2 , SiH_3 , SiH_4 and their cations can be found in the literature [17,18]. Data for SiH_3F [16,19] and Si_2H_5F [20] have also been published, but are included in the tables for comparison. The relevant geometric parameters are gathered in table 2. The tri-coordinate cation, SiH_2F^+ , is a planar molecule of C_{2v} symmetry with a short Si-F bond (1.535 Å versus 1.594 Å in SiH_3F^+). The tetra-coordinate ion, SiH_3F^+ , has one very long Si-H bond (≈ 2.5 Å) and is better described as an $H \cdots SiH_2F^+$ complex. A similar structure has been found for SiH_4^+ [20].

The optimized geometry of $H_3Si-F-SiH_3^+$ at the HF/6-31G* level of calculation (see fig. 1) is linear,

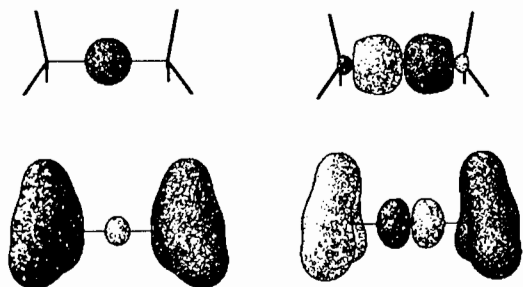


Fig. 2. Valence molecular orbitals of the sigma type in $(SiH_3)_2F^+$.

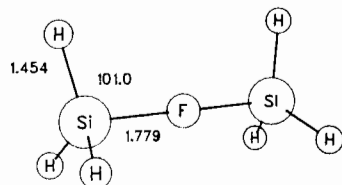


Fig. 1. The optimized geometry for eclipsed $(SiH_3)_2F^+$. The bond lengths are in Å, and the bond angle is in deg.

in contrast to $H_3Si-O-SiH_3$ which is bent ($\theta(Si-O-Si) \approx 144^\circ$ (exp. [21]), $142-154^\circ$ (calc. [22,23])); however, both molecules are very flexible. Only 0.3 kcal/mol are required to bend $H_3Si-F-SiH_3^+$ by 30° , and less than 1 kcal/mol to bend $H_3Si-O-SiH_3$ linear [23]. The SiH_3 groups in $H_3Si-F-SiH_3^+$ are essentially free rotors (barrier of 0.06 kcal/mol at HF/3-21G) with the eclipsed conformation slightly more stable. The Si-F bonds (1.779 Å) are distinctly longer than normal (1.594 Å in SiH_3F and 1.535 Å in SiH_2F^+), consistent with F^+ forming a bridging bond between the two SiH_3 groups. The Mulliken population analysis yields a charge of -0.55 on the F in $H_3Si-F-SiH_3^+$ compared to -0.51 in SiH_3F , indicating that positive charge is located primarily on the SiH_3 groups, rather than on F. The sigma-type valence orbitals, shown in fig. 2, support both the charge distributions and the description of a delocalized, three-center bond.

3.2. Vibrational frequencies

Table 3 lists harmonic vibrational frequencies cal-

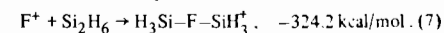
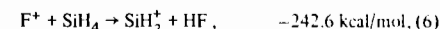
culated at the HF/3-21G level. For molecules containing silicon and fluorine, this level of computation yields frequencies that are 7-8% too high [16] when compared to experimental anharmonic frequencies. This over-estimation of the frequencies is due to the neglect of vibrational anharmonicity and electron correlation in the calculations. In the present study, it is primarily the Si-F stretching modes which are of interest. For the neutral molecules listed in table 3, the calculated Si-F stretching frequencies are 943 cm^{-1} for SiH_3F (875 cm^{-1} obs. [24]) and 925 cm^{-1} for Si_2H_5F . In the cations, the Si-F stretching modes occur at higher frequencies, namely, 1093 cm^{-1} for SiH_2F^+ and 1087 cm^{-1} for SiH_3F^+ .

The calculated frequencies for eclipsed $H_3Si-F-SiH_3^+$ are all real, confirming that the structure is a true minimum. The staggered conformation has an imaginary frequency for the torsion mode, as required for the transition structure for internal rotation. The very low frequency for SiH_3 torsion in the eclipsed structure, 16 cm^{-1} , supports the description of the ion as a nearly free internal rotor. In a similar manner, the low frequency found for the doubly degenerate linear bend, 110 cm^{-1} , is consistent with a linear but very flexible Si-F-Si linkage. There are two modes involving the Si-F stretch, as illustrated in fig. 3. The symmetric stretch at 423 cm^{-1} is Raman-active, and the antisymmetric stretch at 740 cm^{-1} is infrared-active. The symmetric mode in the gas phase ion is likely to be a poor model for active modes in the solid, since the two Si groups move in opposite directions, resulting in a significant increase in the Si-Si distance. On the other hand, the antisymmetric stretch is probably a good model for a vibration in the solid, because it does not involve a change in the

Si-Si distance; however, the use of the $H_3Si-F-SiH_3^+$ frequencies to interpret the spectrum of the ion-implanted solid requires some caution, since the Si-F-Si bridge may be bent in the solid, and many not carry a net positive charge. With these cautions in mind, we can suggest that the metastable B band at 750 cm^{-1} in F^+ implanted amorphous silicon corresponds to the antisymmetric Si-F stretch at 740 cm^{-1} in gas phase $H_3Si-F-SiH_3^+$. Simple force field calculations [9] have been used previously to support a similar identification.

3.3. Energetics

The reactions of F^+ (triplet ground state) with small silicon-containing molecules are highly exothermic, e.g.,



The addition of F^+ to SiH_3 in the gas phase should be quite facile, but the other reactions involve a crossing between a triplet surface for the reactants and a singlet surface for the products. Intersystem crossing should be less of a problem in the solid. While these gas phase reactions are only crude models of possible events in the solid, they do indicate that electronic factors favor the incorporation of F^+ as covalently bonded to silicon.

Some of the primary products can react further. The lower energy unimolecular pathways include:

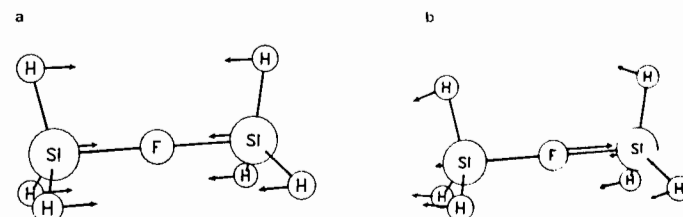
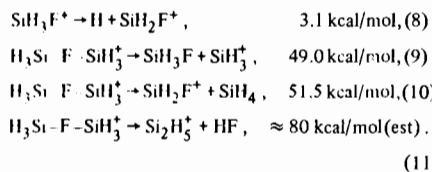
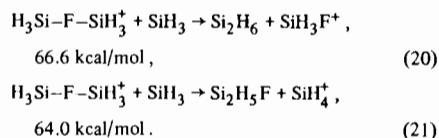
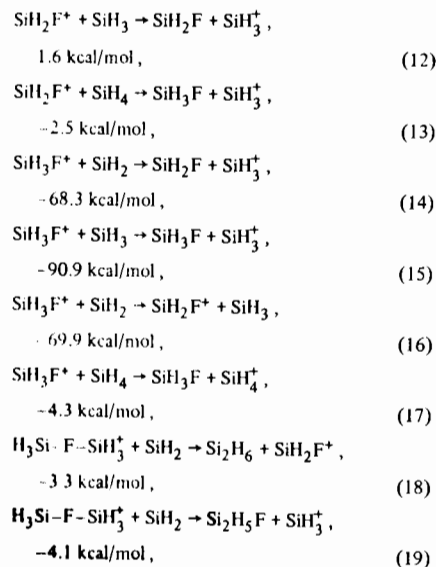


Fig. 3. Si-F stretch modes in $(SiH_3)_2F^+$: (a) Raman-active symmetric stretch at 423 cm^{-1} ; (b) IR-active asymmetric stretch at 740 cm^{-1} .



The small dissociation energy calculated for SiH_3F^+ is in accord with the long Si-H bond and a loose H... SiH_2F^+ cluster. On the other hand, $\text{H}_3\text{Si}-\text{F}-\text{SiH}_3^+$ appears to be rather stable with respect to unimolecular decomposition. This suggests that it may be possible to detect $\text{H}_3\text{Si}-\text{F}-\text{SiH}_3^+$ experimentally under suitable conditions. An analogous ion, $\text{H}_3\text{C}-\text{F}-\text{CH}_3^+$ has been observed by ion cyclotron resonance (ICR) [25] and has a dissociation energy (to $\text{CH}_3\text{F} + \text{CH}_3^+$) of 44 ± 8 kcal/mol.

In the solid, the primary structures formed by F^+ implantation can react further during annealing by atom and charge migration. These processes can be modeled by bimolecular gas phase reactions and include:



The energetics of these reactions indicate clearly that the positive charge is most stable on a tri-coordinated silicon atom (reactions (14)–(16)). Fluorine substitution does not change the stability of the cations significantly (reactions (12) and (17)). There is a slight preference for normal singly bonded fluorine over bridged fluorine (reactions (18) and (19)), provided that the isomerization yields a tri-coordinated cation. This is consistent with the disappearance of the B band associated with the bridged structure on annealing.

4. Summary

(1) The $(\text{SiH}_3)_2\text{F}^+$ ion contains a bridging fluorine in a linear, but very flexible Si-F-Si linkage. The SiH_3 groups are free rotors.

(2) $(\text{SiH}_3)_2\text{F}^+$ appears to be stable with respect to unimolecular decomposition, and should be observable experimentally, similar to its carbon analogue.

(3) $(\text{SiH}_3)_2\text{F}^+$ has an antisymmetric Si-F stretch at 740 cm^{-1} , that is probably a good model for the metastable B band at 750 cm^{-1} observed in F^+ implanted amorphous silicon. The Si-F stretches in non-bridging neutrals and cations are at higher frequencies and may be candidates for the C and/or G bands.

(4) Some bimolecular reactions of $(\text{SiH}_3)_2\text{F}^+$ are slightly exothermic, suggesting pathways for the disappearance of bridging fluorine configurations upon annealing.

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