Fluorinated hydrogenated amorphous silicon alloys. Electronic structure due to SiF_n units and their chains

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A theory for the electronic structure of amorphous fluorinated silicon alloys (a-Si:F) has been discussed by using a cluster-Bethe-lattice method (CBLM). The various silicon-fluorine conformations, e.g., SiF, SiF₂, SiF₃, (SiF)_n, and (SiF₂)_n, in an otherwise perfect tetrahedral network of Bethe lattice discussed earlier by one of the authors in the study of their vibrational excitations have been considered. A realistic tight-binding Hamiltonian considering the interactions up to the second neighbors within the complexes has been employed for calculating the electron energy values of the complexes embedded into the bulk. The local density of states (LDOS) at the F atom and the Si atom to which they bond have been computed both for the s and p orbitals. The F 2p components dominate the local density in the valence-band region in all the configurations. In the case of simple SiF_2 and SiF_3 complexes and in fluorosilane $(SiF)_n$ and $(SiF_2)_n$ chains we observe some extra structure in the density of states which has not been detected in the photoemission data, probably due to the occurrence of topological disorder in the amorphous alloy. The calculated peak positions are in excellent agreement with the available photoemission data. The present study identifies the occurrence of the SiF, SiF₂, and SiF₃ conformations in these alloys. Further, in the study of the electronic structure of the fluorosilane-like configurations $(SiF)_n$ and $(SiF_2)_n$ embedded into the silicon matrix, one observes spiky structures in the electronic density. The smoothened peaks of these spiky structures are still in good agreement with the photoemission intensity assigned to the isolated SiF₂ and SiF_3 units. These results suggest the possible occurrence of the coupled SiF and SiF₂ units in *a*-Si:F alloys in agreement with the results of a similar analysis of the infrared data by our group.

I. INTRODUCTION

Tremendous efforts towards the study of the amorphous silicon (a-Si) pure and doped with impurity atoms such as hydrogen, fluorine, carbon, oxygen, nitrogen, etc. have been made primarily for two reasons. The first is the possible technological applications in thin-film devices and solar photovoltic energy conversion. The second centers on answering fundamental questions about, e.g., the nature of electronic states and electrical transport in amorphous semiconductors.

The possibility of putting an amorphous material into technical applications depends mainly on the knowledge of the structural defects and the role of the impurities present therein. Almost all the physical properties, i.e., electrical, optical, elastic, etc. of the material are drastically influenced by the existence of the vacancies, voids, internal surfaces, topological disorder, etc. The occurrence of the dangling bonds gives rise to a high electron density of states in the optical gap of a semiconductor. The states in the gap are localized, which act as traps leading to low values for the drift mobility and the low recombination times of free carriers. As such amorphous silicon (a-Si) cannot be doped for its use as device.

One can tailor the properties of *a*-Si, inducing chemical modifications, by incorporating impurity atoms such as H, F, O, N, etc. Spear and LeComber¹ and later on Paul *et al.*² showed that the hydrogenated *a*-Si (*a*-Si:H) can be doped substitutionally to achieve *n*-type or *p*-type behavior. The good electronic properties of *a*-Si:H is a

consequence of the passivation of the dangling bonds by H atoms. The density of the states in the gap region reduces from about 10^{20} (eV⁻¹cm⁻³) to values as low as about 10^{15} (eV⁻¹cm⁻³), leading to a sufficiently high carrier lifetime for improved efficiency for solar cells. For highly hydrogenated samples one still detects appreciable electron-spin-resonance (ESR) signals indicating the existence of unpaired electrons. Further, heavy hydrogenation also widens the gap.

Recently, Madan *et al.*³ have reported that the addition of fluorine to *a*-Si:H improves the doping efficiency of the hydrogenated amorphous silicon. Further, the *a*-Si:(F,H) alloys have much better thermal and mechanical stabilities and less photostructural changes compared to the *a*-Si:H alloys. Also, the alloys are highly photoconductive.

Very recently, Tawada *et al.*⁴ have reported the formation of the wide gap-window material by incorporating carbon in *a*-Si and reported an efficiency of more than 8% for *a*-SiC:H/*a*-Si:H hetrojunction structure for solar cells.

All the above properties are a consequence of the type of the silicon network and the local silicon dopant conformations present in the alloy. The local bonding conformations and the structure of the solid leave their signatures in the electronic excitations which can be observed in the electronic spectra. One may thus gain a great insight into the nature of the various matrix-dopant atomic conformations which is the first step in an effort to understand the various physical properties of the alloys.

Theoretical investigations on the electronic states of the amorphous pure or doped systems have been extremely difficult because of the complex nature of the systems, lack of structural information, and the less straightforward correlation between the theoretical results and the available experimental data.

The theoretical calculations of the densities of states become considerably difficult when the periodicity of the system is lost or when the primitive unit cell of a periodic system contains very many atoms. In the past, various approaches to study the vibrational and electronic properties of amorphous materials have been made: (i) calculation of the spectrum of a finite cluster of atoms,⁵ (ii) study of cluster of atoms with quasiperiodic boundary conditions,⁶ (iii) study of the molecular units interacting weakly,⁷ (iv) study of the density of states by statistically averaging the crystalline density of states,⁸ (v) study of exactly solvable mathematical models (Bethe and Husumi lattices),⁹ which have very simple topological properties, and (vi) application of the Bethe-Peierl approximation.¹⁰

Method (i) requires a very large cluster to yield results independent of the boundary conditions. Method (ii) can have some spurious features in density of states due to periodicity, in addition to the drawback of method (i). In spite of the above shortcomings, these approaches consider the local topology exactly. Method (iii) is not suitable for the group semiconductors. In method (iv), one does not consider the real structures for which the short-range order (SRO) and local topology can be considered. Method (v) produces relatively featureless density of states which provides little insight into the problem. Method (vi), although it treats the local environment exactly, cannot distinguish between the different topological arrangements of atoms. A method has been developed which is particularly suited for the studies of the short-range order (SRO) or the short-range disorder (SRD). The usefulness of the method arises from the fact that the properties of small regions of atoms can be isolated. It is based on a reasonable model, which is exactly solvable, avoids the difficulties of the other methods, is very easy to handle numerically and can, in principle, by successive approximations, be made to converge exact results.¹¹

The method named the cluster-Bethe-lattice method (CBLM) involves treating part of an infinitely connected network of atoms exactly as a cluster and representing the effect of the rest of the environment by connecting a Bethe lattice to the surface of the cluster. The Bethe lattice is an infinite network of atoms with the same coordination number devoid of any ring structure. It provides a natural background upon which the individual properties of the cluster are studied.

Some experimental studies have recently been made on amorphous silicon-hydrogenated fluorine alloys. Shimada *et al.*¹² have reported the results of their infrared absorption measurements on *a*-Si containing only fluorine. The infrared data for *a*-Si:F:H alloys has also been obtained.^{3,13-17} These studies have led to the theoretical study^{18,19} of the vibrational excitations in these alloys.

Quite recently, Gruntz *et al.*²⁰ have performed the x-ray and ultraviolet photoemission measurements on the amorphous fluorinated silicon samples. They have reported a number of peaks arising from the fluorine atoms depending on its concentration. The results were in overall agreement with the theoretical densities of states reported by Ching,²¹ using a method of orthogonalized linear combination of atomic orbitals (OLCAO). However, there were discrepancies observed between the theory and the experiment, especially in the spectra of SiF₃ conformation where four peaks have been assigned to SiF₃ against the three peaks obtained in the calculation. Also, the effects of the existence of other likely configurations such as $(SiF_2)_n$ or coupled $(SiF)_n$ units were not investigated.

The study of the effects of the possible occurrence of the perfluorosilanes $(SiF_2)_n$ or the coupled SiF_n units on the electronic structure of the amorphous silicon is warranted by the fact that some of the high-frequency peaks seen in the infrared spectra of the *a*-Si:F alloys cannot be interpreted only in terms of the isolated SiF_n units. These extra peaks may arise from the vibrational excitations of the $(SiF_2)_n$ chains or coupled SiF units, as has been investigated by our group.¹⁸ In fact, our group has observed that similar high-frequency localized phonon modes may originate from the isolated SiF₃ unit or from the coupled SiF₂ units. Also, the same may be true for the case of two interacting SiF units and the isolated SiF₂ unit.

Recently, our group has been engaged in a detailed and comprehensive study of the vibrational and electronic excitations in the hydrogenated fluorinated amorphous silicon alloys using the cluster-Bethe-lattice method. We showed that most of the available infrared absorption measurements performed on the a-Si:F:H alloys can be understood in terms of the simple five atom complexes of F and H atoms.¹⁸ In a subsequent article¹⁸ (hereafter referred to as II), we have discussed the effect of the (SiF), and $(SiF_2)_n$ chainlike configurations on the vibrational excitations of a-Si and noted that some of the peaks seen in the infrared data which remained unexplained earlier on the basis of five atom units may originate from the chainlike configurations.¹⁸ Similarly, we have found that in pure hydrogenated silicon alloys, several peaks seen in the infrared and Raman measurements can be understood on the basis of the occurrence of the simple five atoms and/or of the silanelike $(SiH)_n$ and $(SiH_2)_n$ configurations. A report on our study of the vibrational and electronic properties of the mixed F and H configurations would be the subject matter of subsequent papers (referred to as III and IV).

In the present investigations, we consider all types of the silicon-fluorine conformations present in the amorphous silicon and study their effects on the electron density of the bulk silicon. The amorphous silicon is simulated by a Bethe lattice and the effects of the various clusters are investigated in the cluster-Bethe-lattice method. We find that the recent photoemission spectra of fluorinated amorphous silicon alloys can very well be understood on the basis of the occurrence of the isolated units of SiF, SiF₂, and SiF₃ complexes. The same identification is supported by the study of the vibrational excitations of these complexes by our group.¹⁸ However, extra structure in the electronic density of states arise from the interacting SiF and SiF₂ units. This structure may escape a photoemission detection of even high sensitivity.

In Sec. IIA, we present in brief an outline of the linear-combination-of-atomic-orbitals (LCAO) method.

The cluster-Bethe-lattice method is also discussed here (Sec. II B). The calculations for the electron energy values for the various isolated SiF_n complexes in the silicon matrix are given in Sec. III. We investigate the energy excitations of the $(SiF)_n$ and $(SiF_2)_n$ chains in Sec. IV. Some observed extra structure may be interpreted in terms of the available photoemission data. The main conclusions are contained in Sec. V.

II. THEORY

Before studying the behavior of any complex present in a matrix, it is imperative to understand the nature of the excitations of the complex by itself. One may then easily follow the effects of a matrix on the excitations of the complex present in the solid. We have thus made a study of the molecular excitations using the linear combination of atomic orbitals (LCAO) method and the elementary excitations of various complexes embedded into a matrix of Bethe lattice. We present the details of the CBLM here and the details of molecular calculation appear elsewhere.²²

A. LCAO method

We employ here the LCAO method for the polyatomic systems. Here, the individual one-electron wave functions $\psi_{\gamma}(\vec{r})$ of the polyatomic molecule at position \vec{r} are expanded in atomiclike basis functions $\Phi_{\alpha}(\vec{r})$ centered on the atomic position *j*,

$$\psi_{\gamma}(\vec{\mathbf{r}}) = \sum_{\alpha,j} F_{\alpha j}^{\gamma} \Phi_{\alpha}(\vec{\mathbf{r}} - \vec{\mathbf{R}}_{j}) \tag{1}$$

or, equivalently

$$\psi_{\gamma}(\vec{\mathbf{r}}) = \sum_{\alpha,j} F^{\gamma}_{\alpha j} \Phi_{\alpha j}(\vec{\mathbf{r}}) \; .$$

Here \overline{R}_j denotes the lattice position vector for the site *j*; α specifies the various orbitals at a site; γ designates the various molecular orbitals and $F_{\alpha j}^{\gamma}$ are the coefficients of the linear combination. One needs to solve the eigenvalue problem

$$\sum_{\alpha',j'} H_{\alpha\alpha'}(\vec{R}_j - \vec{R}_{j'}) - E^{\gamma} S_{\alpha\alpha'}(\vec{R}_j - \vec{R}_{j'}) F^{\gamma}_{\alpha'j'} = 0$$
(2)

with

$$H_{\alpha\alpha'}(\vec{R}_{j} - \vec{R}_{j'}) = \langle \Phi_{\alpha j} | \underline{H} | \Phi_{\alpha' j'} \rangle , \qquad (3)$$

where E^{γ} is the electron energy, <u>H</u> is the one-electron Hamiltonian matrix of the system, and the overlapping integral is given by

$$S_{\alpha\alpha'}(\vec{R}_j - \vec{R}_{j'}) = \langle \Phi_{\alpha j} | \Phi_{\alpha' j'} \rangle .$$
⁽⁴⁾

In an *ab initio* calculation, one must choose the orbitals $\Phi_{\alpha j}(\vec{r})$ and then evaluate the multicenter integrals of Eqs. (3) and (4). However, as such the method is recognized to be too cumbersome for accurate calculations. Slater and Koster²³ suggested that the LCAO matrix elements $H_{\alpha\alpha'}(\vec{R}_j)$ can be treated as parameters to be fit to the calculated energy levels. Further, according to a

theorem, 23,24 orthonormal set of LCAO orbitals could be defined rigorously, such that

$$S_{\alpha\alpha'}(\mathbf{R}_i) = \delta_{\alpha\alpha'} \delta_{i0} . \tag{5}$$

However, the matrix elements of the true Hamiltonian are to be replaced by those of a non-Hermitian pseudo-Hamiltonian.

The dimension of the full Hamiltonian matrix can be reduced by employing the group-theoretical methods for a system possessing some symmetry. The necessary symmetrized linear combinations of the atomic orbitals have been constructed for the C_{3v} , C_{2v} , and T_d point groups and are presented elsewhere.²²

B. Cluster-Bethe-lattice method

A Bethe lattice has been used for the calculation of the density of states. The local Green's function at any site can be calculated exactly. The density of states of the Bethe lattice is smooth and featureless, and, therefore, the local environment of the atom leaves its signatures on the density of the energy states in a cluster-Bethe-lattice calculation.

One may define the Green's-function operator denoted by \underline{G} for a system by

$$\underline{G} = (\epsilon \underline{I} - \underline{H})^{-1} , \qquad (6)$$

where ϵ is energy of an excitation, <u>I</u> is the unit operator, and <u>H</u> is the Hamiltonian operator of the system. It may be rewritten as a Dyson equation in matrix form as

$$(\epsilon \underline{I} - \underline{H}^0)\underline{G} = \underline{I} + \underline{V}\underline{G} \tag{7}$$

with

$$\underline{H} = \underline{H}^0 + \underline{V} . \tag{8}$$

Here \underline{H}^0 is the diagonal matrix containing the energies of the noninteracting orbitals at the same site and \underline{V} is the interaction Hamiltonian matrix between the orbitals lying on the different atoms, e.g., at the nearest-neighboring or the second neighboring sites.

Once \underline{G} is known, various properties of the system such as the electronic density of states can be calculated easily. The matrix elements of Eq. (7) can explicitly be written as

$$\epsilon \langle i | \underline{G} | j \rangle = \underline{I}_{ij} + \sum_{k=1}^{4} \langle i | \underline{V} | k \rangle \langle k | \underline{G} | j \rangle .$$
(9)

Equation (9) can be solved exactly for a Bethe lattice. The infinite set of coupled equations can be reduced to a small set by utilizing the symmetries of the Bethe lattice, in the form of the transfer matrices or the effective fields. We may represent a four-dimensional vector in the space of orbitals by a dot. In the open structure of the Bethe lattice, every dot can be transformed into another dot by a fixed set of transformations. Also, any two nearest-neighboring dots are connected to each other by only one self-avoiding path. One can define a transfer-matrix \underline{t}_{ji} at site *i* for each inequivalent line (*j*) joining any two nearest-neighboring dots. The whole lattice is replaced by only one dot interacting via the four transfer matrices. By definition the Green's function at one site should be iden-

(12)

tically equal to one with the entire Bethe lattice.

One obtains the following two closed equations for the transfer matrices in a pure solid:

$$\underline{t}_{ji} = (\epsilon \underline{I}_{jj} - \underline{H}_{jj}^{0} - \underline{\overline{F}} + \underline{v}_{ij}^{T} \underline{\overline{t}}_{ij})^{-1} \underline{v}_{ij}^{T}$$
(10)

and

$$\overline{\underline{t}}_{ij} = (\epsilon \underline{I}_{ii} - \underline{H}_{ii}^{0} - \underline{F} + \underline{v}_{ij}\underline{t}_{ji})^{-1}\underline{v}_{ij}$$
(11)

with

$$\underline{F} = \sum_{j} \underline{v}_{ij} \underline{t}_{ji}$$

and

$$\overline{\underline{F}} = \sum_{i} \underline{v} \,_{ij} \overline{\underline{t}}_{ij} \; .$$

Here $\underline{v}_{ij} = \langle i | \underline{V} | j \rangle$. The Green's function between the two more distant sites *i* and *k* is related to that between the two nearer ones *i* and *j* by

$$\underline{G}_{ki} = \underline{t}_{kj} \underline{G}_{ji} , \qquad (13)$$

where \underline{t}_{kj} is the transfer matrix or the effective field at the site j along the direction of atom k. The equations (10) and (11) may be solved self-consistently for the evaluation of the eight transfer matrices \underline{t}_{ij} and \underline{t}_{ji} .

The local Green's-function matrix for the site i is then given by

$$\underline{G}_{ii} = (\epsilon I_{ii} - \underline{H}_{ii}^{0} - \underline{F})^{-1}.$$
(14)

The local density of states at the atomic site (i) is

$$\rho_i(\epsilon) = (-1/\pi) \operatorname{Im} \operatorname{Tr}(\underline{G}_{ii}) , \qquad (15)$$

where Im $Tr(\underline{G}_{ii})$ is the imaginary part of the trace of the Green's-function matrix at the site *i*.

III. CALCULATION AND RESULTS FOR SiF_n COMPLEXES

A. Evaluation of parameters

We consider the nearest-neighbor and the secondneighbor Si-F and the F-F interactions. The electrons of each atom are described by one *s* orbital and three *p* orbitals (p_x, p_y, p_z) . We need to know the six interaction integrals for each type of bond. They are as follows:

$$E_{s} = \langle s \mid \underline{H} \mid s \rangle, \quad E_{p} = \langle p \mid \underline{H} \mid p \rangle,$$

$$U = \langle s \mid \underline{H} \mid s' \rangle, \quad V = \langle p_{x} \mid \underline{H} \mid p_{x'} \rangle,$$

$$X = \langle s \mid \underline{H} \mid p' \rangle, \quad T = \langle p_{x} \mid \underline{H} \mid p_{y'} \rangle.$$
(16)

Here the primes specify the atomic orbitals lying on the neighboring site of the reference atom. The sets (E_p, E_s) and (E'_p, E'_s) stand for the atomic energy levels of F and Si atoms, respectively. Similarly, the set of the interaction parameters (U, V, X, T) denote the nearest-neighbor interactions for the Si-F bond and the set (U', V', X', T') for the Si-Si bond. For the second-neighbor interactions, these parameters are (U'', V'', X'', T'') for the F-F and (U''', V''', X''', T''') for the Si-F bond.

The values of the interaction parameters for the Si-Si

bond in an amorphous material are taken over from its crystalline form. In the tight-binding description of the electronic states in terms of short-range interactions of electrons centered on the nearest-neighboring atoms, one determines the necessary interaction parameters by fitting the energies at the various symmetric points of the Brillouin zone. For details, we refer to Chadi and Cohen.²⁵ The parameters used in the present calculations are shown in Tables I and II. The s- and p-orbital energies for the various atoms are taken over from the atomic values calculated by Herman and Skillman²⁶ barring the s-orbital energy for Si, which is 0.78 eV higher here (Table I). The values are determined after fitting the electron energy bands to the photoemission²⁷ and optical data,²⁸ and the pseudopotential results of Chelikowsky and Cohen.²⁸ Chadi²⁹ and Allan *et al.*³⁰ have obtained the values of these parameters for Si. We prefer to use the set by Joannopoulos which generates a broader valence band and a smaller band gap for the Bethe lattice.

For the silicon-fluorine complexes one should know the values of the various two-center integrals of Eq. (3). We consider here all the nearest-neighbor interactions and the second-neighbor interactions for the F atoms. For the evaluation of the necessary parameters for the Si—F and F-F bonds, we employ the available x-ray photoelectron data of Perry and Jolly³¹ for the SiF₄ molecule.

The energies of the involved molecular orbitals (MO) along with the main atomic components contained in each electronic level are compared with the experimental data in Table III. A remarkably good agreement is observed between the calculated and the experimental results. The present assignment is in agreement with that of the earlier workers.^{31,32}

The electronic energies of the various molecular orbitals along with the main atomic orbital components for the Si₅, Si₄F, Si₃F₂, and Si₂F₃ complexes have been computed and given elsewhere.²² The levels arising from the Si–Si bonds appear mainly in the energy interval -2.0 to -16.0 eV. The number of the 2s- and 2p-levels due to F atoms increase with the number of F atoms. The F2s levels are well separated from the other levels. The various F2p levels lie in the region -16.0 to -22.0 eV in these molecules. It is also noted that the energy levels corresponding to the 2s- and 2p- levels of F atoms are undisturbed by the addition of more Si atoms to the complexes, although there is an increase in the number of levels due to Si–Si bonds, an observation which is later seen to

TABLE I. Atomic orbital energies used for the free molecules and for the cluster-Bethe-lattice calculation, in eV, measured with respect to vacuum and the top of the valence bond, respectively.

	In free molecule		In Bethe lattice		
Orbitals	Si	F	Si	F	
Ep	-6.52	-17.00	1.20	-9.28	
$\dot{E_s}$	-12.77	-35.80	- 5.05	-28.08	
	(-13.55) ^a				

^aThis value is different from the atomic value of Herman and Skillman (Ref. 26).

TABLE II. Values of the first-neighbor and second-neighbor matrix elements for the interaction matrix for the different bonds, in eV.

Interaction	Bond	U	X	V	T
First- neighbor interactions	Si—Si Si—F		1.01 2.94	1.73 3.73	0.66 0.34
Second- neighbor interactions	F—F F—Si	3.47 1.735	-0.13 -0.065	0.85 0.295	0.60

remain true for these complexes when they are embedded into the silicon matrix.

B. Cluster Bethe lattice

1. Bulk a-Si

First, the calculations are performed for the electronic density of a Bethe lattice simulating the amorphous silicon matrix using Eqs. (6)–(15). The energies are measured with respect to the top of the valence band. All the atomic orbital energies are thus shifted by 7.72 eV towards the higher energy side. The values of the tightbinding interaction parameters for the crystalline silicon, as shown in Table II, are used for obtaining the density of states for amorphous silicon. For all the other nearestneighbor and the next-nearest-neighbor bonds between Si and the alloy atoms or for bonds between the alloy atoms themselves, the interaction parameters obtained for the SiF₄ molecule are used in the cluster-Bethe-lattice calculation.

The electronic density of states for the bulk silicon for s and p orbitals is shown in Fig. 1. The density at the bottom both of the valence and the conduction bands arises mainly from the s-type states, whereas the p states appear at the top of the valence band and also at the bottom of the conduction band. However, there is a mixing in the middle region of the valence band. The energy gap is wider as compared to the actual value. This is true for all the calculations performed for a Bethe lattice where the



FIG. 1. Electronic density of states for Si-Bethe lattice with their s and p components.

widths of the bands are seen to be smaller due to the short-range nature of the atomic interactions.

2. Isolated SiF_n complexes in CBLM

Using the parameters of Tables I and II for the nearest-neighbor and the next-nearest interactions of various bonds, the CBLM has been used to calculate the electron density of states for the various complexes. The results are depicted in Figs. 2–4 and the main peaks in the electron density are shown in Table IV. The calculated results have also been compared with the lone available x-ray and ultraviolet photoemission data of Gruntz *et al.*²⁰ They have analyzed their measured data in terms of the occurrence of the simple SiF, SiF₂, SiF₃, and SiF₄ configurations based on the fluorine-induced chemical shift of the Si core levels.

The density at the F atom and at the Si atom bonded to the F atom (Si^*) is shown in Fig. 2. The density of the F atom is contributed mainly by the *p* electrons. At Si, the

TABLE III. Energy values for the various molecular orbitals for SiF_4 molecule, in eV. AO denotes atomic orbital.

Serial No.	Molecular orbital	Calculated energy	Experimental energy (Ref. 31)	Main AO components
1	\mathbf{A}_1	-40.60	-40.6	Si 3s,F 2s
2	\mathbf{F}_{2}	-40.39	-39.27	F 2s,Si 3p
3	\mathbf{A}_1	-21.40	-21.4	F 2p,F 2s,Si 3s
4	\mathbf{F}_2	- 19.18	-19.4	F 2p,Si 3p,F 2s
5	E	-18.10	-18.1	F2p
6	\mathbf{F}_2	-17.63	-17.4	F 2p, Si 3p
7	\mathbf{F}_1	-16.40	16.4	F 2 <i>p</i>
8	\mathbf{F}_2	-1.49		Si 3 <i>p</i> ,F 2 <i>p</i>
9	A ₁	3.94		Si 3s,F 2s,F 2p



FIG. 2. Electronic density of states for SiF conformation.

contributions of s electrons is seen almost throughout the band region, although small in magnitude. The calculated density spectrum has been shifted by 1.8 eV towards the higher-energy side in order to match the peaks with the photoemission data. There arise two peaks in the valence band due to s-p orbitals in the low-energy region; one at -11.2 eV and the other due to p orbital towards the high-energy side at -8.9 eV. The two peaks are not too localized, but delocalized as appreciable density due to them can be seen at the Si^{*} atom [Fig. 2(b)]. The location of the peaks and their separation are in excellent agreement with the experimental data. There is a marked decrease in the electron density in the vicinity of the gap on both ends, i.e., at the top portion of the valence band and at the bottom of the conduction band.

For the SiF₂ complex (Fig. 3), in the valence band, there are in all five peaks arising mainly from the *p* electrons except the lowest one, which is a *s*-*p* mixed one. The calculated spectrum has been shifted merely by 0.9 eV towards the higher-energy side for comparison with the experimental data. The average of the three peaks appearing at -8.35, -8.65, and -9.65 eV is located at -8.9 eV,



FIG. 3. Electronic density of states for SiF_2 conformation.



FIG. 4. Electronic density of states for SiF₃ conformation.

which is in agreement with the photoemission data where a broad peak at -9.2 eV has been detected. The two peaks in the region -8.0 to -9.0 eV are highly localized at F atoms. The nearest-neighboring silicon atom (Si^{*}) does not have any significant density at these high-energy peaks [Fig. 3(b)]. On the other hand, the low-energy peaks are somewhat delocalized and the corresponding states are seen on the coupled silicon atom Si^{*} [Fig. 3(b)]. Also, the density at the edges of the gap is reduced further.

For the SiF₃ complex (Fig. 4), in the valence band, one obtains six peaks arising from the *p* orbitals except the lowest one which is again an *s*-*p* mixed peak. The calculated spectra has not at all been shifted to make a comparison with the photoemission data. The highest two peaks at -13.5 and -11.75 eV are localized only to the F atoms [Fig. 4(a)], whereas the densities corresponding to the lower four peaks at -11.05, -10.05, -9.4, and -8.7 eV are also observed at the silicon atom [Fig. 4(b)]. The photoemission data has revealed only four peaks at -13.4, -11.4, -9.8, and -9.0 eV. The average of the

TABLE IV. Peaks of the valence band in the density of state curves. All energies are in eV.

Conformation	Calculated	Experimental (Ref. 20
Si:F	-11.2	-11.3
	-8.9	- 8.9
Si:F ₂	-12.4	- 12.5
	-10.3	-10.2
	-9.65	
	8.65	-9.2
	-8.35	
Si:F ₃	-13.5	-13.4
	-11.75 -11.05	-11.4
	10.05 9.4	-9.8
	-8.7	-9.0

peaks at -11.75, and -11.05 eV is -11.4 eV, a value seen in the experimental data. Further, the average of the peaks at -10.05 and -9.4 eV turns out to be -9.7 eV, again in agreement with the experimental one at -9.8 eV. One thus finds a very close agreement between the theory and the experiment.

There is no electron density in the gap in contrast to the result of Ching.²¹ The density in the neighborhood of the two edges of the gap is further reduced.

To sum up it is noted that the density at the edges of the energy gap shows a decreasing trend with the incorporation of more F atoms. In the photoemission data of Gruntz *et al.*,²⁰ the top of the valence band has been found to recede proportional to the amount of fluorine incorporated.

Also, the peaks in all the conformations are derived almost exclusively from F2p states. This has been noted by Gruntz *et al.*²⁰ in their photoemission data where the fluorine-induced structures are very similar in the He II and XPS spectra.

Finally, the calculated results for the electron density for the SiF, SiF₂, and SiF₃ complexes are in excellent agreement with the photoemission data. However, the experimental peaks are somewhat broader compared to the calculated ones which indicate towards the occurrence of topological disorder present in the alloy. The variations in the Si-F bond lengths, the deviation of the values of the bond angles from the tetrahedral ones and the variation in the dihedral angles are expected to be present in the amorphous alloys.

IV. $(SiF)_n$ AND $(SiF_2)_n$ CHAINS

Until now we discussed the simplest silicon-fluorine conformations SiF_n expected to be present in the fluorinated Si samples. However, there are several other bigger complexes like the chains of SiF and SiF_2 units, i.e., $(\text{SiF})_n$ and $(\text{SiF}_2)_n$ which may also occur in these alloys. There is some evidence from the infrared measurements on the *a*-Si:F alloys, where some extra very-high-frequency localized modes associated with the stretching vibrations of Si-F bonds have been detected. They have been interpreted in terms of the vibrations of the coupling of more than



FIG. 5. Electronic density of states for (SiF)₂ conformation.



FIG. 6. Electronic density of states for $(SiF_2)_n$ conformation.

one SiF and SiF₂ units by our group.¹⁸ In the present section we study the electronic structures of the chain configurations and investigate how far the new electronic structure is compatible with the available photoemission data. We have calculated the electronic local density of states for the (SiF)_n and (SiF₂)_n configurations and present them in Figs. 5–8. The peak positions are shown in Tables V and VI.

A. $(SiF)_n$ chains

First, we study the two interacting SiF units, i.e., (SiF)₂ embedded into the silicon matrix. The computed local density of states at the F and Si atoms is shown in Figs. 5(a) and 5(b), respectively. The local density at the F atom is compared with the photoemission intensity due to the isolated SiF₂ unit assigned by Gruntz et al.²⁰ There now appear four peaks in the calculated density of the F atom because of the splitting of the corresponding two peaks of an isolated Si-F unit (see Table V). However, the splitting of the s-p state at -11.3 eV lying in the low-energy region is higher (-12.0, -10.5) eV as compared to that for the pure F 2p state lying towards the high-energy side (-9.0, -8.55 eV). This splitting of ~ 0.45 eV may not be observable in the photoemission experiment. Apart from the fine structure, the three experimental peaks assigned earlier to the SiF₂ unit are in good qualitative and quantitative agreement with the calculated peaks of the coupled SiF units. In the local density at the Si^{*} atom [Fig. 5(b)],

TABLE V. Comparison of the calculated peak positions in the $(SiF)_2$ chain with the photoemission data in *a*-Si:F alloys measured in eV.

Serial	Calcula	Calculated energy		Photoemission data		
No.	SiF	(SiF) ₂	SiF	SiF_2		
1		-11.95	A	- 12.5		
2	-11.2		-11.3			
3		-10.55		-10.2		
4		-9.0		-9.2		
5	- 8.9		- 8.9			
6		-8.55				



FIG. 7. Electronic density of states for $(SiF_2)_3$ conformation.

there appears an extra weak peak near ~ -5.5 eV and an enhanced Si 3p orbital density at the top of the valence band. However, the -8.5 eV peak disappears at the Si^{*} atom.

B. $(SiF_2)_n$ chains

The calculated peak positions for the $(SiF_2)_n$ chains are shown in Table VI. We now turn to the study of the two coupled SiF₂ units. The calculated density at the F and Si atoms are depicted in Figs. 6(a) and 6(b), respectively. There are overall seven peaks at the F atom and five peaks at the Si atom. The two highest peaks are quite localized and are missing at the Si^{*} atom. Again apart from the fine structure seen in the calculated data, the electronic density is in overall good agreement with the experimental photoemission intensity of both the SiF₂ and SiF₃ units where four peaks have been detected.

For the longer $(SiF_2)_3$ chain, the local density of states at the exterior and interior F atoms has been shown in Figs. 7(a) and 7(b), respectively. The number of calculated peaks increases and the computed spectrum is in qualita-



FIG. 8. Electronic density of states for $(SiF_2)_4$ conformation.

tive agreement with the photoemission data of the SiF_3 unit [Fig. 7(a)]. The same is true for the local density at the interior F atom [Fig. 7(b)]. It is to be noted that there appears density in the gap region of the bulk silicon near the top of the valence band.

For the $(SiF_2)_4$ chain, the density at the exterior F atom [Fig. 8(a)] and at the interior F atom [Fig. 8(b)] reveal more structure as expected. However, barring the spiky structure, all the main peaks are in very good agreement with the photoemission data for SiF₃, a result seen above for the $(SiF_2)_3$ chain. Also, similar to the $(SiF_2)_3$ chain, there is electronic density of states in the gap region.

To sum up, we thus find that the expected spiky structure arises due to the splitting of the peaks arising from the interaction of the various SiF and SiF₂ units. This structure might appear in a more refined photoemission measurement or in other types of experiments. Broadening of the peaks may also occur on account of the topological disorder in amorphous silicon and the spiky structure may be smoothened. The smoothened peaks are in very good agreement with the available photoemission data.

Serial		Calculated energy			Photoemis	sion data
No.	SiF ₂	$(SiF_2)_2$	$(SiF_2)_3$	$(SiF_2)_4$	SiF_2	SiF_3
1			-13.25	-13.4		-13.4
		-12.95				
2	-12.4		-12.35	-12.6	-12.5	
3		-12.0		-12.1		
4			-11.85	-11.8		-11.4
5		-10.6	10.65	- 10.7		
6	-10.3	-10.35	- 10.3	-10.3	- 10.2	
7		-10.0	-10.0	- 10.0		-9.8
8						
9	-9.65	-9.65	9.65	9.65	0.2	0.0
10	-8.65	- 8.6	8.6	-8.60	-9.2	9.0
11						
12	-8.35	-8.35	-8.35	-8.35		

TABLE VI. Comparison of the calculated peak positions in the $(SiF_2)_n$ chains with the photoemission data in *a*-Si:F alloys, measured in eV.

V. CONCLUSIONS

Using the cluster-Bethe-lattice method, we have studied the electronic density of the simplest silicon-fluorine configurations SiF_n and also that of the fluorosilane chainlike $(SiF)_n$ and $(SiF_2)_n$ configurations. The calculated electronic density for the various SiF_n complexes is in excellent agreement with the available photoemission data. All the experimentally observed peaks can be interpreted in terms of the presence of simple units. The splitting in the energy levels arising from the interaction of the two or more SiF and SiF₂ units causes spiky structures in the electronic density. This extra structure may only be detected in a photoemission experiment of high sensitivity or in other types of experiments. The smoothened density due to these chains is, however, again in excellent agreement with the photoemission intensity assigned to the isolated SiF₂ and SiF₃ units. These results support our assignment of some extra peaks seen in the infrared measurements to the coupled SiF_n units by our group elsewhere.¹⁸

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