

CHEMICAL BONDING STRUCTURE OF AMORPHOUS SILICON-FLUORINE ALLOYS

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Chemical bonding structure of a-Si:F is examined by IR absorption and XPS studies. Bonding states of Si-F fragments are clarified by IR spectra due to Si-F_n stretching and bending modes and the chemical shift in XPS spectra. The absorption bands corresponding to IR-forbidden TO and LO phonon modes in crystal Si, grow with F content. Highly electronegative F atoms not only induce large charge transfer from Si to F but also strongly polarize Si-Si bonds.

I. Introduction

Amorphous silicon containing fluorine (a-Si:H:F [1], a-Si:F [2]) is receiving a great deal of attention as a solar cell material having high thermal and photochemical stabilities. However, the chemical bonding structure in this material has not been revealed in detail. Generally, Si-F amorphous alloys can be expected to have various bonding configurations of fluorine to silicon, such as Si-F, Si-F₂, and Si-F₃, and the fluorine atom incorporated will affect the Si-Si network which mainly determines the fundamental electronic structure of this alloy.

In order to clarify the chemical bonding structure of this material, infrared absorption (IR) and X-ray photoelectron spectroscopy (XPS) were performed on amorphous silicon containing only fluorine, a-Si:F, with a wide range of fluorine content.

II. Experimental

Samples were prepared on silicon wafers by reactive sputtering of a high-purity silicon crystal in SiF₄ or a mixture of SiF₄-Ar gas under a total pressure of 0.5 Pa with an rf (13.56 MHz) input power density of 5 W/cm². The growth rate was 15-20 Å/s, depending on the partial pressure of SiF₄. The temperature of the stainless steel substrate holder, T_S, was kept constant.

The IR spectra were taken by a Hitachi type 225 and a Digilab FTS 20-C Fourier transform spectrometers. The XPS spectra were taken with a Vacuum Generator ESCA 3 system under the base pressure of less than 4 x 10⁻⁹ Pa.

III. Results and Discussion

Figure 1 shows the relative transmittance of a-Si:F alloys in the range of 450-1400 cm⁻¹ (Fig. 1 (a)) and in the range of 200-600 cm⁻¹ (Fig. 1 (b)). No absorption peaks were found in the range of

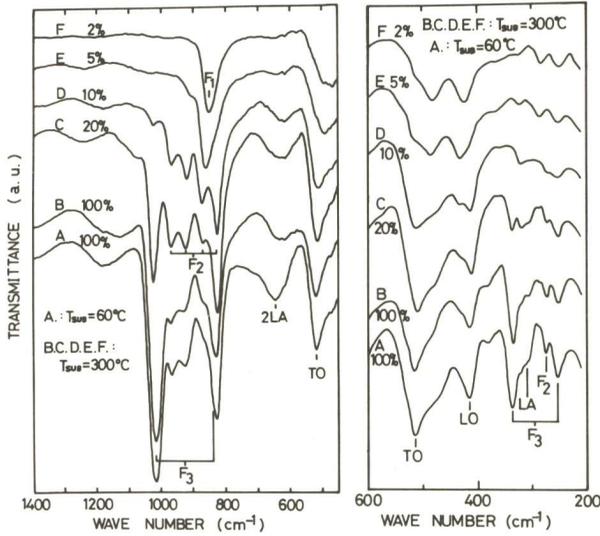


Fig. 1 IR absorption spectra of a-Si:F with various SiF₄ contents in a gas mixture

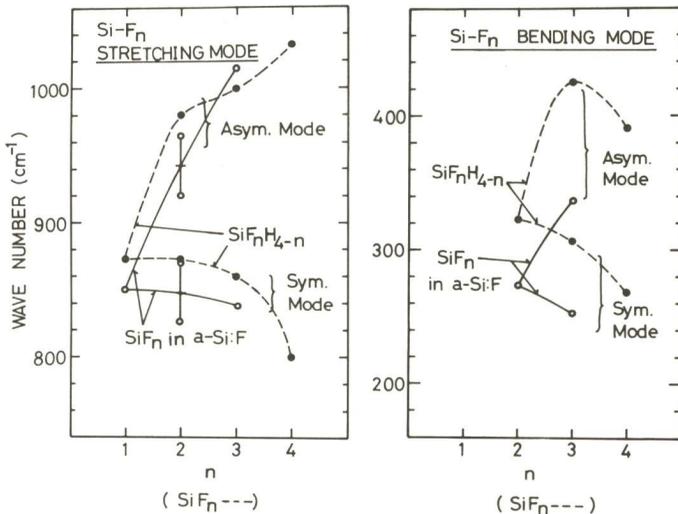


Fig. 2 n dependences of Si-F_n vibration frequencies in SiF_nH_{4-n} molecules (broken lines) and in a-Si:F (solid lines)

1100-4000 cm⁻¹. As the amount of fluorine atoms incorporated increases, seven sharp absorption peaks appear successively in the 820-1020 cm⁻¹ region in addition to three peaks in the 250-350 cm⁻¹ region. These two groups of peaks are found to correspond to the Si-F_n bond stretching and bond bending modes, respectively, by comparison with the Si-F_n vibration modes in fluorosilane molecules SiF_nH_{4-n} (n=1, 2, 3, 4). The broken lines in Fig. 2 (a) and (b) show the symmetric and asymmetric Si-F_n stretching and bending vibration frequencies in SiF_nH_{4-n}. For n=1, there is only one stretching mode and no bending mode.

Therefore, it is reasonable to assign the single band at 850 cm⁻¹ as seen in sample F of Fig. 1 (a) to the nondegenerate Si-F stretching mode, since the smallest content of SiF₄ in the gas mixture would result in the formation of isolated SiF bonds in the amorphous films. As the SiF₄ content in the gas mixture increases, SiF₂ and/or SiF₃ bonds will become dominant. By comparing the frequencies of the Si-F_n vibration modes of SiF_nH_{4-n} to those of the growing peaks in the range of 820-1020 cm⁻¹ as seen in samples D, C, B and A of Fig. 1 (a) and in the range of 250-350 cm⁻¹ in C, B and A

of Fig. 1 (b), each peak can be reasonably assigned to a mode of SiF₂ or SiF₃ as shown by the solid lines in Fig. 2 (a) and (b). Details of the assignments of Si-F_n stretching vibration modes were discussed in a separate paper [3].

In the case of SiF₂, antisymmetric and symmetric modes have two frequencies each. This means that the SiF₂ segments form a (SiF₂)_n

polymer-like chain similar to the well-known $(\text{SiH}_2)_n$ polymer-like chain in a-Si:H alloys. Existence of the $(\text{SiF}_2)_n$ polymer leads to the prediction that the pair band for $(\text{SiF}_2)_n$ bending mode frequency of 273 cm^{-1} should appear in the SiF_n bending mode region. It seems to overlap with the symmetric bending mode of SiF_3 at 252 cm^{-1} .

Frequency shifts to the lower energy side for all modes in these alloys except the asymmetric SiF_3 stretching mode compared with the vibration frequencies for $\text{SiF}_n\text{H}_{4-n}$ molecules seen in Fig. 2 can be explained in terms of the electronegativity difference between

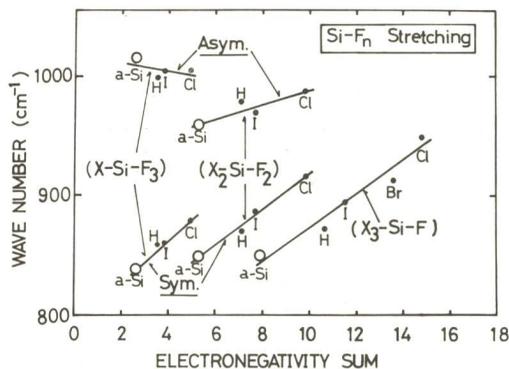


Fig. 3 Electronegativity sum of X atoms vs Si-F_n stretching vibration frequencies in $\text{SiF}_n\text{X}_{4-n}$ molecules

Si and H, which are similar to that in the case of a-Si:H [4]. Figure 3 shows the Si-F_n stretching vibration frequencies in $\text{Si}_n\text{X}_{4-n}$ molecules as a function of Sanderson's electronegativity sum of X_{4-n} atoms, H, I, Br and Cl. For a-Si:F alloys, the atom should be considered to be Si. The observed frequencies in a-Si:F and the electronegativity sums of Si_{4-n} atoms are shown by the open circles. These points fall right on the extrapolated lines determined by the vibration frequencies in $\text{SiF}_n\text{X}_{4-n}$ molecules, where X is H, I, Br and Cl. Similar considerations can be done for bending vibration modes. The resulting assignments of corresponding peak frequencies are summarized in Table 1.

Table 1. Assignments of the IR absorption bands observed in a-Si:F

	Assignment	Frequency (cm^{-1})
Si-F ₃	*Asymmetric doubly degenerate stretching	1015
	*Symmetric stretching	838
Si-F ₂	*Antisymmetric stretching	965, 920
	*Symmetric stretching	870, 827
Si-F ₁	*Stretching	850
Si-F ₃	*Asymmetric doubly degenerate bending	337
	*Symmetric bending	252
Si-F ₂	*Bending	273 (252?)
Si-Si(-F)	*2LA	650
	*TO	515
	*LO	420
	*LA	310

As the SiF_4 content approaches zero, only a broad absorption remains in the range of 400-500 with a tail to 300 cm^{-1} . Comparison with the energy distribution of phonon modes of crystalline silicon shows this broad absorption to be attributable to the Si-Si vibration modes. The absorption bands at around 650, 515, 420, and 310 cm^{-1} seem to correspond to the 2LA, TO, LO and LA modes in the crystalline concept. As seen in Fig. 1 (b), this absorption becomes

stronger and sharper with increasing SiF_4 content in the gas mixture. This can be understood by considering that the Si-Si vibration, which is infrared-inactive in crystalline silicon, becomes allowed by the fluorine-induced polarization of the Si-Si bond. In the case of Si-H alloys, the enhancement of this absorption is weak. This fact suggests that incorporation of atoms with large electronegativity strongly modifies the Si-Si network and also changes its electronic structure.

In Fig. 4, the XPS spectra of a-Si:F alloys prepared with different SiF_4 contents in the gas mixture are shown in the binding energy region of the Si-2p core level. The main peak at 98.7 eV corre-

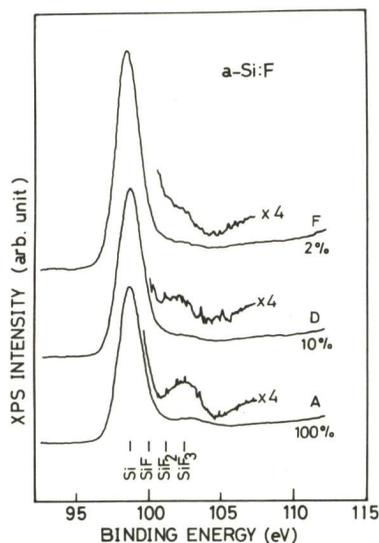


Fig. 4 Si-2p XPS spectra of a-Si:F with various SiF_4 contents in a gas mixture

sponds to the 2p level of silicon surrounded by four silicons. As surrounding silicons are replaced by atoms whose electronegativities are larger than that of silicon, the Si-2p level chemically shifts to the high energy side. In XPS spectra, the peak intensity of O-1s in the surface thin oxidized layer formed in air during sample transfer from the sputtering chamber to the XPS analyzer is nearly same for all alloys, while that of F-1s becomes large with increasing partial pressure of SiF_4 in the sputtering gas. The same amount of O or F would produce a similar intensity satellite peak to the higher energy side of the Si-2p main peak. As seen in Fig. 4, intensity of satellite peak at around 102 eV becomes strong with increasing partial pressure of SiF_4 in the sputtering gas. This means that the satellite peak is mainly fluorine-bonded Si-2p level. This chemical shift coincides with the estimated value from electronegativity difference between Si and F, as shown in the bottom of Fig. 4. Sample A with the satellite band at 102.2 eV corresponding to SiF_3 shows strong SiF_3 absorption in the IR spectra, as mentioned in the IR results. With decreasing SiF_4 content in the gas mixture, the satellite band becomes weak and shifts to the low

energy side. This behavior is consistent with the results that sample D dominantly shows SiF_2 IR absorption and sample F shows SiF absorption, in contrast with sample A showing strong SiF_3 absorption.

IV. Conclusion

The structure of the amorphous silicon-fluorine alloys was examined by IR absorption and XPS spectroscopies. Chemical bonding structures of Si-F_n segments and the effects of incorporated fluorine on the Si-Si network were revealed.

V. References

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