PROC. 15TH INT. CONF. PHYSICS OF SEMICONDUCTORS, KYOTO, 1980
J. PHYS. SOC. JAPAN **49** (1980) SUPPL. A p. 1241–1244

INFRARED AND PHOTOEMISSION SPECTRA OF AMORPHOUS FLUORINATED SILICON

L. Ley, H.R. Shanks[+], C.J. Fang[*], K.J. Gruntz and M. Cardona

Max-Planck-Institut für Festkörperforschung
7000 Stuttgart 80
Federal Republic of Germany

Si-F, Si-F_2, Si-F_3 and Si-F_4 species have been identified in a-Si:F,H films through their vibrational frequencies as measured with ir-spectroscopy. Upon annealing some of the Si-F transform into Si-F_4. Gas evolution experiments show that F is stable in a-Si:F up to the crystallization temperature. Fluorine 2p induced states between 9 and 14 eV below the valence band maximum have been identified by photoemission.

I. Introduction

Madan et al. [1] have suggested that the addition of fluorine to a-Si:H (a-Si:H,F) results in a material with a doping efficiency higher than that of the merely hydrogenated substance (a-Si:H). Furthermore, the room temperature conductivity of their phosphorus doped fluorinated material had a value of $\sim 1\ \Omega^{-1}\ \mathrm{cm}^{-1}$, not previously obtained in amorphous hydrogenated silicon.

Here we report ir absorption and photoemission measurements on a-Si:H,F films. From these measurements we deduce the bonding configurations of F in the a-Si network. The photoemission measurements reveal directly the position of the fluorine induced states in the a-Si valence bands. The thermal stability of hydrogen and fluorine was investigated in annealing and differential gas evolution experiments.

II. The Preparation of Fluorinated a-Si

Films of fluorinated a-Si were prepared by RF sputtering from a c-Si target in a gas mixture containing argon, hydrogen, and silicon tetrafluoride (SiF_4) onto a substrate held at 65°C. The specific power level was $\sim$8.8 W/cm^2. A flow of argon gas was adjusted so as to maintain a pressure of 10^{-2} torr with the unthrottled pump. The flow rates of H_2 and SiF_4 were similarly adjusted to yield pressures in the range from 5×10^{-4} to 2×10^{-3} torr. The deposition rate obtained with these parameters was approximately 1µm/h. The samples investigated were between 1µm and 2µm thick.

III. Results and Discussion

Fig.(1) shows the infrared spectrum of an a-Si:H,F film obtained with a ratio of 5 for the SiF_4/H_2 partial pressures in the sputtering gas. The infrared absorption coefficient, $\alpha(\omega)$, was calculated from the transmission using the procedure of Brodsky et al. [2]. Table I summarizes the positions and assignments of peaks observed in the ir-spectra of 10 films prepared with different SiF_4/H_2 ratios.

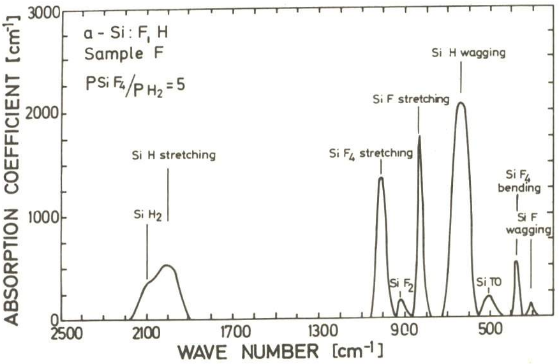

Fig. 1

The infrared spectrum of a-Si:F,H prepared at room temperature

The hydrogen induced bands are readily identified in analogy with the corresponding absorption peaks in hydrogenated a-Si (a-Si:H) [2]. The frequencies are shifted downwards by 15 cm^{-1} (stretching) and 10 cm^{-1} (wagging) in the fluorinated samples. The remaining lines are fluorine related vibrations. The bands at 1010 cm^{-1} and at 380 cm^{-1} always occur together with a constant intensity ratio $I(1010)/I(380) = 5.0 \pm 0.5$. We ascribe them to the bond-stretching (1010 cm^{-1}) and bond-bending (380 cm^{-1}) vibrations of SiF_4 molecules imbedded in the a-Si matrix during the deposition process. The average Si-F bond-stretching frequency (longitudinal + transverse) in solid SiF_4 is 1013 cm^{-1} and the average bond-bending frequency is 385 cm^{-1} [3]. The cross sections of the two bands in crystalline SiF_4 [4] give a ratio $\Gamma(1013)/\Gamma(385) = 5.2$ also in good agreement with the corresponding intensity ratio measured in all our films.

Table I

wave number	2085	1985	890-840	630		(cm^{-1})
mode	Si-H$_2$ stretch	Si-H stretch	Si-H$_2$, Si-H$_3$ bending	Si-H, Si-H$_2$ wagging		
wave number	1010	930-920	828	510	380	300 (cm-1)
mode	SiF$_4$ stretch	Si-F$_3$;Si-F$_2$ stretch	Si-F stretch	Si TO (F-induced)	SiF$_4$ bending	Si-F,Si-F$_2$ wagging

The Si-F stretching frequencies for a number of methyl and fluorine substituted silanes cover a range from 1013 cm^{-1} in SiF_4 to 858 cm^{-1} in $FSiH_2CH_3$ [5]. When plotted versus the electronegativity sum of the substituted groups, these frequencies extrapolate to a mode at 810 cm^{-1} expected for the Si-F stretch frequency in a-Si [6]. The closest band observed in our spectra is that at 828 cm^{-1} which we ascribe consequently to that mode. This assignment agrees with that made by others [1,7,8]. The frequency of the Si-F wagging mode is estimated as 291 cm^{-1} from the stretching frequency using the ratio of the bond-stretching to bond-bending force constants from SiF_4 [4]. The band closest to this value at 300 cm^{-1} in Fig.(1) is therefore identified with that mode. The stretching modes for Si-F$_2$ and Si-F$_3$ configurations are expected to lie between those of SiF_4 and Si-F. The asymmetric line at 930 cm^{-1} is thus the most likely candidate.

Shimada et al. [8] assign a prominent line at 1015 cm^{-1} to the asymmetric doubly degenerate Si-F$_3$ stretching band. They position the corresponding symmetric band at 838 cm^{-1}. We do not find lines at either of these positions. But if we suppose that our lines at 1010 cm^{-1} and 828 cm^{-1} are identical with their Si-F$_3$ bands we expect an intensity ratio of two for these lines on the basis of their degeneracy. Since a bond at 827 cm^{-1} attributed to Si-F$_2$ by Shimada et al. could conceivably contribute to our line at 828 cm^{-1} as well, this ratio would be an upper limit. In Fig.(2) spectra are shown with an intensity ratio I(1010)/I(828) >2 which exclude the interpretation of the 1010 cm^{-1} line as due to Si-F$_3$.

Finally, the peak in the transmission spectra of Fig.(1) at 510 cm^{-1} lies within the TO band of the a-Si lattice (for c-Si the peak in the density of TO states occurs at 490 cm^{-1}). While this mode is ir-inactive in the non-polar Si network, the addition of the highly electronegative F should induce enough charge transfer in its neighborhood to ir-activate this mode in a-Si:F and shift its frequency to 510 cm^{-1}. The intensity of this band scales with the Si-F and Si-F$_2$ vibrational modes but not with the SiF$_4$ modes.

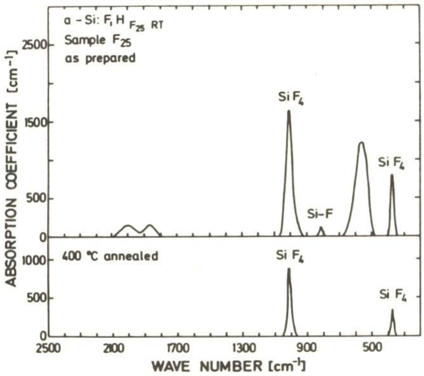

Fig. 2

Ir-spectra of a-Ge$_x$Si$_{1-x}$:F before and after annealing

The hydrogen and fluorine content of the films as a function of annealing temperature, T$_a$, was monitored by gas evolution experiments and by ir-spectroscopy after a number of isochronal annealing steps. Hydrogen evolves in two stages. In the samples containing no fluorine evolution rates peak around 350°C and around 550°C. In the fluorinated sample the evolution maxima are shifted up to ∿390°C and 610°C, respectively. Three fluorine containing species could be identified in the mass spectra of all fluorinated films: F (mass 19), HF (mass 20), and SiF$_4$ (mass 104). All three evolve in one narrow peak at 680°C, just below the crystallization temperature of a-Si.

Figure (3) depicts the integrated absorption strengths of various ir bands as a function of T$_a$. The hydrogen bands show the annealing behaviour observed earlier in non-fluorinated a-Si:H samples [9]. The Si-F stretching band at 830 cm^{-1}, and the F-induced TO mode of the silicon network at 510 cm^{-1} decrease monotonically with increasing annealing temperature at very much the same rate. The Si:F$_4$ bands (1010, 380 cm^{-1}) increase (slowly initially, more rapidly above 300° to 350°C) and peak around 530°C. Beyond 600°C they fall off rapidly and at 700°C no fluorine containing bands could be detected in the ir-spectra. Combining these results with the gas evolution data we conclude that a transformation from Si-F to Si-F$_4$ takes place.

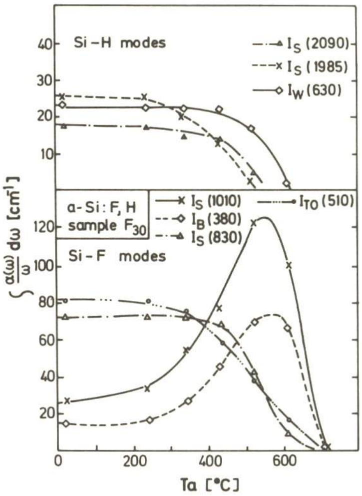

Fig. 3

Intensity of ir-absorption bands as a function of annealing temperature

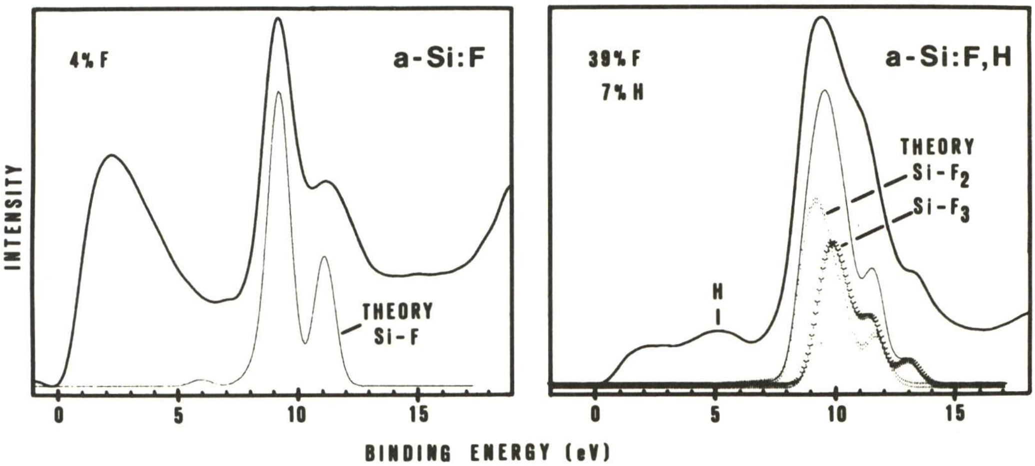

Fig. 4

Photoemission spectra of two fluorinated a-Si films

The photoemission spectra ($\hbar\omega$ = 40.8 eV) for two films containing 4%F and 39%F are shown in Fig.(4). The film with 4%F exhibits a doublet of F 2p induced states at 9.1 and 11.2 eV below E_F. The corresponding local density of states (LDOS) for a Si-F configuration calculated by Ching [10] is seen to reproduce the experimental result quite nicely after a rigid shift of 2.7 eV to lower binding energies has been applied. The 39%F film has a three peaked structure with 9.3, 11.2, and 13.2 eV binding energies. A superposition of the calculated Si-F$_2$ and Si-F$_3$ LDOS is again in good agreement with our results with the same 2.7 eV shift. From the position of the Fermi level in our spectra we conclude that the a-Si:F films are p-type. The top of the valence bands is apparently much less affected by the incorporation of F than by the addition of H [11].

References

1) A. Madan and S.R. Ovshinsky: J. Non-Cryst. Solids 35-36 (1980) 171.
2) M.H. Brodsky, M. Cardona and J.J. Cuomo: Phys. Rev. B 16 (1977) 3556.
3) E.R. Bernstein and G.R. Meredith: J. Chem. Phys. 67 (1977) 4132.
4) P.N. Schatz and D.F. Hornig: J. Chem. Phys. 21 (1953) 1516.
5) H. Kriegsman: Zeitschrift für anorganische und allgemeine Chemie 294 (1958) 113.
6) C.J. Fang, L. Ley, H.R. Shanks, K.J. Gruntz and M. Cardona: Phys. Rev. (1980).
7) M. Konagai and K. Takahashi: Appl. Phys. Lett. 36 (1980) 599.
8) T. Shimada, Y. Katayama: Jap. J. Appl. Phys. 19 (1980) L265.
9) H.R. Shanks, C.J. Fang, L. Ley, M. Cardona, F.J. Demond and S. Kalbitzer: Phys. Stat. Sol. (1980).
10) **W.Y. Ching**:Amorphous and Liquid Semiconductors, W. Paul, M. Kastner editors (North-Holland, New York 1980), p. 61.
11) B. von Roedern, L. Ley, M. Cardona, F.W. Smith: Phil. Mag. B 40 (1979) 433.

[+] on leave from Ames Laboratory, U.S.D.O.E., Ames, Iowa, U.S.A.

[*] on leave from Chinese University of Science and Technology, Beijing, People's Republic of China.