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# Amorphous Silicon-Carbon-Fluorine Alloy Films

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## Amorphous silicon-carbon-fluorine alloy films

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A new amorphous semiconductor alloy system  $\text{Si}_x\text{C}_x\text{F}_y$  has been prepared by rf sputtering of polycrystalline SiC in an Ar+SiF<sub>4</sub> atmosphere. Dark conductivity and optical absorption of thin films are measured as functions of F concentration. Infrared spectra indicate a preferential attachment of fluorine to carbon over silicon. The bonded fluorine concentration is estimated to be as high as 40 at. %. The principal reststrahlen band shifts to higher frequencies and appears to sharpen with the increase of fluorine concentration. Fluorinated films are observed to be resistant to high-temperature annealing.

## I. INTRODUCTION

Preparation and properties of amorphous silicon carbide films were first reported<sup>1</sup> in 1974 followed by a detailed investigation<sup>2</sup> of electrical properties and the annealing behavior of sputtered films. The effect of hydrogen on these properties was also investigated.<sup>3-5</sup> A better coordination of the binary random network on incorporation of hydrogen was observed. Recently, fluorine has attracted a great deal of attention as a terminator of dangling bonds.<sup>6-8</sup> A higher thermal stability of amorphous materials has been achieved by terminating unsatisfied bonds with fluorine atoms. We report the preparation and properties of a new amorphous semiconductor alloy system,  $\text{Si}_x\text{C}_x\text{F}_y$ . Infrared spectra of stretching and bending fundamentals of Si-F and C-F bonds were recorded by absorption spectroscopy. Electrical conductivity and optical-absorption edge as functions of fluorine content were investigated. The dark conductivity decreases by a few orders of magnitude and the band gap increases with increasing fluorine content. The amount of fluorine in the alloy was determined from the integrated intensities of Si-F and C-F stretching-mode bands. Films with as high as 40 at. % of fluorine have been prepared. Infrared-absorption spectra indicate a preferential attachment of fluorine to carbon over silicon. The effects of annealing on incorporated fluorine content and dark conductivity of this ternary alloy system were also studied.

## II. EXPERIMENTAL

Amorphous Si-C-F alloy films were prepared in our laboratory by rf sputtering at a constant power of 200 W on water-cooled substrates. An intrinsic polycrystalline silicon carbide target (99.99% SiC),

100 mm in diameter and 10-mm thick, was used in an oil-pumped vacuum system evacuated to a base vacuum of 0.66 mPa. The sputtering was done in a pure (99.999%) Ar + SiF<sub>4</sub> atmosphere at a fixed argon pressure of 1.33 Pa. Partial pressures (0–0.08 Pa) of SiF<sub>4</sub> were chosen as a deposition parameter. The distance between the target and the substrate was 5 cm. The rate of sputtering varied between 0.07 and 0.11 nm s<sup>-1</sup>. Silicon to carbon ratio in amorphous Si-C-F alloys was determined by electron probe microanalysis (EPMA) measurements and was within 5% of the stoichiometric target material composition at all fluorine levels. Infrared transmission and reflection were measured in the region 200–3500 cm<sup>-1</sup> with a Perkin-Elmer model 580B (ratiometric) spectrophotometer. For infrared measurements the samples were deposited on polished single-crystal silicon substrates, slightly wedged (~0.7°) so as to avoid interference fringes.

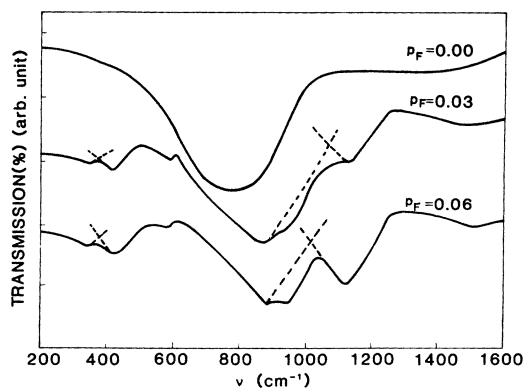


FIG. 1. Infrared spectra of amorphous  $\text{Si}_x\text{C}_x\text{F}_y$  alloys at different fluorine compositions.  $p_F$  represents partial pressure of SiF<sub>4</sub> in the sputtering atmosphere.

TABLE I. Assignments of the infrared-absorption bands observed in Si-C-F alloys at different fluorine compositions.

Material	SiF <sub>4</sub> partial pressure	Assignment	Frequency (cm <sup>-1</sup> )
Amorphous	0.00	Si-C stretching	790
Si-C-F alloys	0.01	Si-C stretching	850
rf sputtered	0.03	Si-C stretching	870
at 200 W	0.06	Si-C stretching	885
		C <sub>3</sub> Si-F stretching	960
		C <sub>2</sub> SiF <sub>2</sub> stretching	
	0.01	$\begin{array}{c} \text{F} \\ \diagdown \quad \diagup \\ \text{C}_2\text{Si} \\ \diagup \quad \diagdown \\ \text{F} \end{array}$ bending	350
	0.03		
	0.06		
		Si <sub>3</sub> C-F stretching	1120
		Si <sub>2</sub> CF <sub>2</sub> stretching	
		$\begin{array}{c} \text{F} \\ \diagdown \quad \diagup \\ \text{Si}_2\text{C} \\ \diagup \quad \diagdown \\ \text{F} \end{array}$ bending	430

The samples investigated were between 1.0- and 1.5- $\mu\text{m}$  thick. Samples appear smooth and shiny when viewed under a microscope. Samples were found to react mildly to atmospheric moisture when exposed over a period of 1 month. Scanning electron microscopy did not exhibit any surface structure down to 1000 Å. Molybdenum electrodes were sputtered on the films, the separation between the electrodes being 1.0 mm. The dark conductivity was measured in the temperature range of 100–400 K *in situ* under high vacuum ( $\sim 0.1$  mPa). A Chromel-Alumel thermocouple monitored the temperature of the film. The voltage source was made up of a 5.4-V mercury cell. No field dependence of the conductivity was observed in the range of the field employed. The absorption-edge measurements were done using a Spex double-beam spectrophotometer. The uncertainty in the measurements of the absorption coefficient is estimated to be within  $\pm 2.0\%$  in the energy range available. Annealing was carried out in a quartz tube in a variable temperature furnace under inert argon atmosphere.

### III. RESULTS AND DISCUSSION

The amorphous nature of the films and their fluorine content have been ascertained by infrared

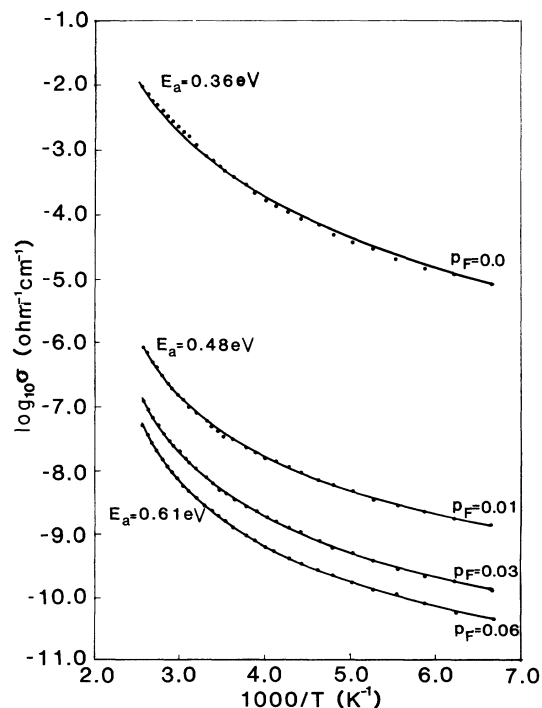


FIG. 2. Dark conductivity as a function of temperature for samples with different fluorine contents.

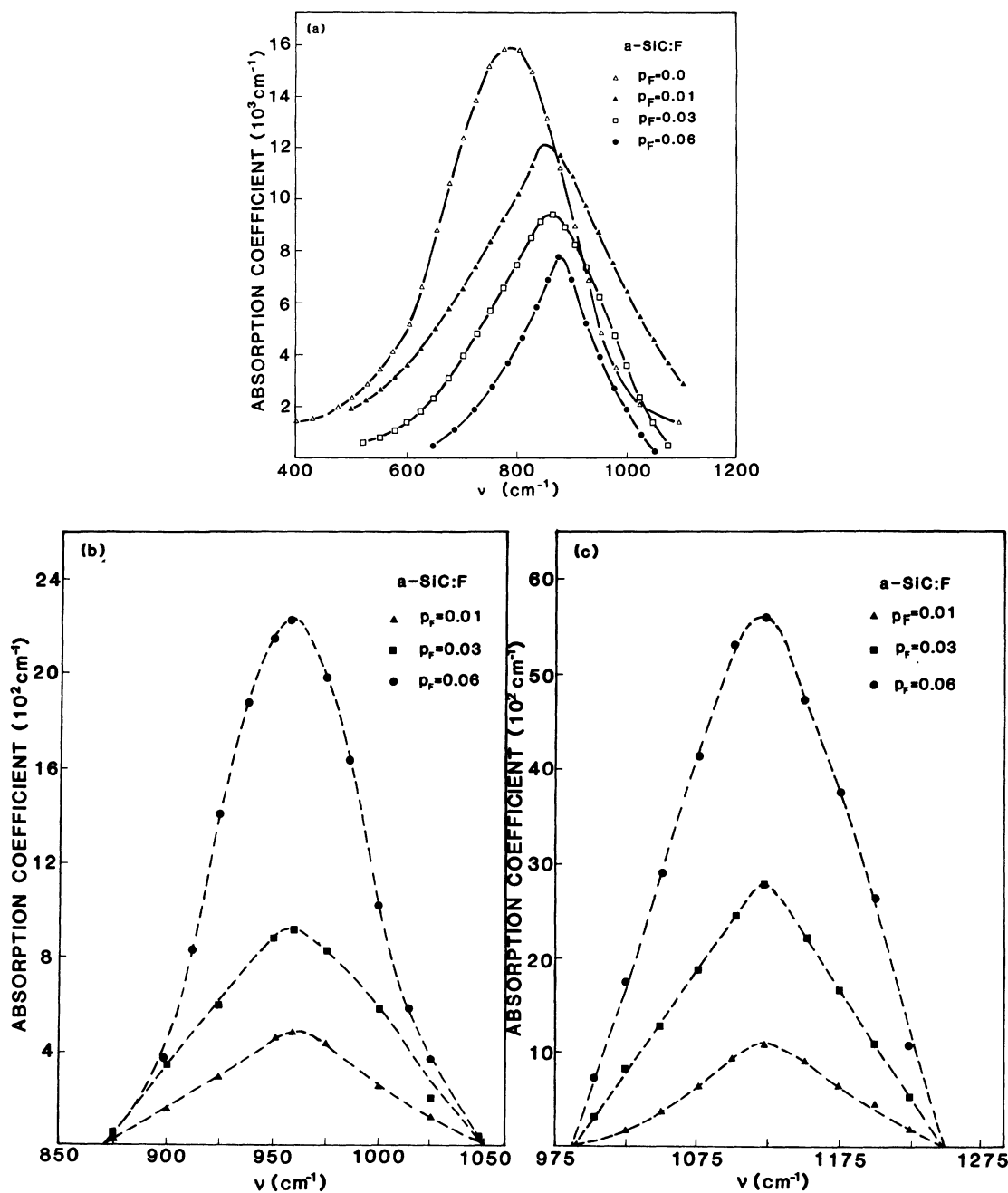


FIG. 3. Infrared-absorption coefficient of various vibrational modes at different fluorine concentrations: (a) Si-C stretching mode, (b) Si-F stretching mode, (c) C-F stretching mode.

spectroscopy. Figure 1 shows the infrared spectra of the amorphous Si-C-F alloys at different fluorine composition. One significant feature is that the principal reststrahlen band of SiC at  $790 \text{ cm}^{-1}$  is shifted continuously to higher frequencies and it appears to sharpen with increasing fluorine content. As the partial pressure of  $\text{SiF}_4$  in the sputtering atmosphere is increased to 6%, the fluorine-induced

reststrahlen frequency shifts to higher energy by 12% and the halfwidth of the band decreases by 38%. The band at  $960 \text{ cm}^{-1}$  is attributed to Si-F stretching in  $\text{C}_2\text{SiF}_2$  and  $\text{C}_3\text{SiF}$  configurations by comparison with the Si-F stretching-band frequency<sup>9</sup> ( $948 \text{ cm}^{-1}$ ) in  $\text{Cl}_2\text{SiF}_2$  and  $\text{Cl}_3\text{SiF}$ . The presence of two fluorine atoms on a common silicon atom and their relative motion is confirmed by the

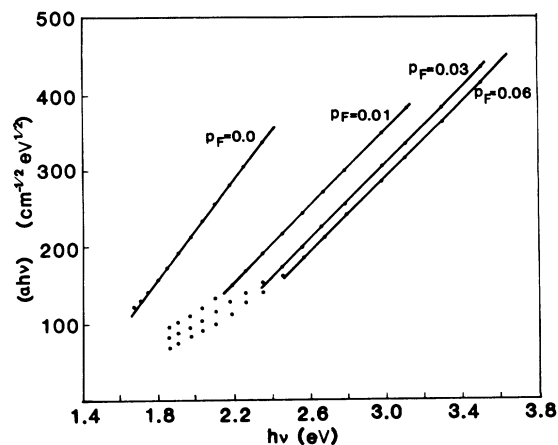


FIG. 4. Room-temperature absorption edge of amorphous  $\text{Si}_x\text{C}_x\text{F}_y$  alloys at different fluorine levels.

deformation-mode frequency at  $350\text{ cm}^{-1}$ . Likewise the band at  $1120\text{ cm}^{-1}$  is the stretching-band frequency of C-F bonds in  $\text{Si}_2\text{CF}_2$  and  $\text{Si}_3\text{CF}$  configurations. This agrees well with the C-F stretching-mode frequency<sup>10</sup> of  $1110\text{ cm}^{-1}$  in  $\text{I}_2\text{CF}_2$ . A normal coordinate analysis yields a frequency<sup>11</sup> of  $1100\text{ cm}^{-1}$  for C-F stretching mode in  $\text{>C-F}$ . The band at  $430\text{ cm}^{-1}$  is assigned to a F-C-F bending mode. The assignments are summarized in Table I. The infrared spectra showed no detectable presence of oxygen or nitrogen in the films. Sputtered films of  $\alpha\text{-Si:H}$  and other alloys are, however, known to contain  $\sim 0.1$  at. % of oxygen. This amount of oxygen, to a certain extent, may influence the electrical properties of the films but in the face of  $\sim 40$  at. % of fluorine such effects are expected to be insignificant.

#### A. Dark conductivity

Figure 2 shows the variation of the dark conductivity with temperature for various samples with different fluorine contents. The parameter  $p_F$  represents the partial pressure of  $\text{SiF}_4$  in the sputtering atmosphere. As calculated later, the at. % of incorporated fluorine is found to increase with increasing  $p_F$  (see Fig. 3). At temperatures higher

than room temperature, the conductivity curves could be approximated by the general expression  $\sigma = \sigma_0 \exp(-E_a/kT)$ . Owing to a slight departure from linearity of the curves even at high temperatures, a least-squares fit of the first six data points at high temperatures are used to calculate activation energy. The activation energy gap  $E_a$  is found to increase with increasing fluorine concentration as shown in Fig. 2. The preexponential factor lies between  $4.5 \times 10^2$  and  $7.0 \times 10^2$  for all fluorinated samples. We consider  $E_a$  and  $\sigma_0$  as experimental parameters relating samples with different F content, since their significance as real material parameters is uncertain. The difference between the measured conductivity at low temperatures and the extrapolated straight-line fit of the high-temperature region could be attributed to the hopping between localized states. The continuous curvature of the data points might, however, also suggest that a hopping between localized states is playing an important role at all temperatures. The room temperature conductivity tends to saturate at higher fluorine levels.

#### B. Absorption edge

The transmission and reflection measurements were made near the principal absorption edge and the absorption coefficient was calculated within an error bar of  $\pm 2.0\%$ . The optical pseudogap  $E_g$  is obtained from the straight-line fit of  $(\alpha h\nu)^{1/2}$  plotted against  $h\nu$  (Fig. 4) assuming the relation  $\alpha h\nu = B_0(h\nu - E_g)^2$ . The straight-line fit yields  $E_g = 1.35\text{ eV}$  for the unfluorinated sample and it increases to  $1.80\text{ eV}$  for the sample with the highest fluorine concentration. At lower photon energies, the absorption spectrum tails off, indicating the presence of localized gap states. The optical pseudogap widens on incorporating fluorine, possibly due to the removal of localized states from the gap.

#### C. Fluorine estimation

The absorption coefficient for the Si-C reststrahlen band is calculated from the infrared transmission data as shown in Fig. 3(a). The peak

TABLE II. Atomic concentration of different constituents in amorphous  $\text{Si}_x\text{C}_x\text{F}_y$  alloys.

Material	$\text{SiF}_4$		Atomic density ( $10^{22}\text{ atom cm}^{-3}$ )			Si-F ( $10^{22}\text{ cm}^{-3}$ )	C-F ( $10^{22}\text{ cm}^{-3}$ )	% of F		Density ( $\text{g cm}^{-3}$ )	
	partial pressure	Si	C	F	At. % F			bonded to Si	bonded to C		
Amorphous	0.00	4.83	4.83	0.00	0.00	0.00	0.00	0.0	00.0	00.0	3.213
Si:C:F	0.01	4.45	4.45	0.76	0.27	0.48	7.8	36.3	63.7	3.198	
alloys	0.03	3.76	3.76	1.90	0.58	1.32	22.1	30.4	69.6	3.174	
rf sputtered at 200 W	0.06	2.74	2.74	4.17	1.20	2.97	43.1	28.7	71.3	3.139	

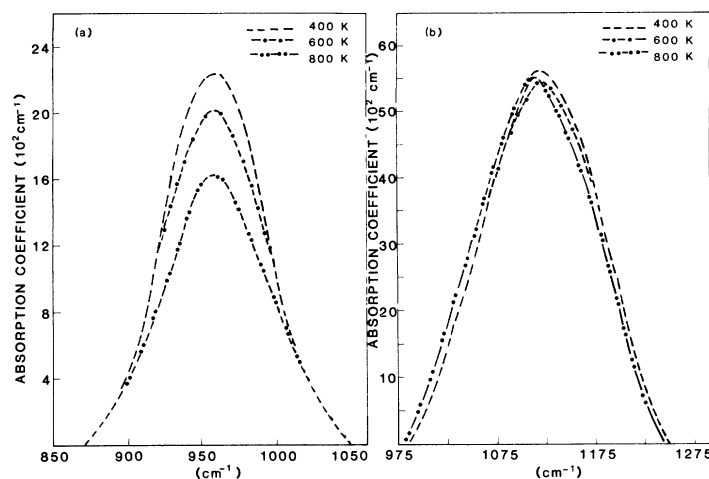


FIG. 5. Infrared-absorption coefficient at different annealing temperatures showing: (a) Si-F stretching mode, (b) C-F stretching mode.

absorption goes down by  $\sim 52\%$  at the highest fluorine concentration. It is worthwhile to note that the Si-C stretching frequency suffers a blue shift when compared to the long-wavelength TO-mode frequency ( $790\text{ cm}^{-1}$ ) of crystalline SiC. The increase in the number of Si-F and C-F bonds in the sputtered films with the increase of the partial pressure of  $\text{SiF}_4$  in the sputtering atmosphere is evident from Figs. 3(b) and 3(c). In order to obtain the total number of Si-F and C-F bonds in the alloys, we have calculated the absolute absorption intensity of a single bond from the absorption spectrum of the corresponding gaseous fluorides ( $\text{SiF}_4$  or  $\text{CF}_4$ ). The absolute absorption intensity  $A$  of a single Si-F or a C-F stretching bond in  $\text{SiF}_4$  or  $\text{CF}_4$ , expressed in  $\text{cm}^{-1}/\text{cm atm}$ , is given by<sup>12</sup>

$$A = \frac{\pi}{4c^2} \left[ \frac{\delta\mu}{\delta Q_{\text{str}}} \right]^2,$$

where  $\mu$  is the vector dipole moment of the molecule,  $Q$  is the normal coordinate for the particular vibration, and  $c$  is the velocity of light. The value of the bond dipole derivate ( $\delta\mu/\delta Q$ ) for the stretching vibration in  $\text{SiF}_4$  and  $\text{CF}_4$  is assumed to be  $\pm 167.4$

and  $\pm 219.8$  esu, respectively.<sup>13</sup> However, since the local field at any point inside a solid is different from the applied field, the magnitude of  $A$  for a bond inside an amorphous solid will be lower compared to the gaseous phase. A local field correction factor  $L$  is introduced in the equation

$$A = \frac{\pi}{4Lc^2} \left[ \frac{\delta\mu}{\delta Q_{\text{str}}} \right]^2.$$

$L$  represents the enhancement of the macroscopic field within a medium of homogeneous dielectric constant  $\epsilon$ .  $L$  is calculated in terms of the dielectric constant as given by<sup>14,15</sup>

$$L = \frac{(1+2\epsilon)^2 \epsilon^{1/2}}{9\epsilon^2}.$$

The value of the dielectric constant is assumed to be 10.2 in the present work.<sup>16</sup>

The number of bonds  $N$  per unit volume of an alloy is related to the integrated band intensity as

$$N = \frac{4Lc^2}{\pi(\delta\mu/\delta Q)^2} \int_{\omega_1} \alpha(\omega) d\omega,$$

TABLE III. Effect of annealing on fluorine content of amorphous fluorinated silicon carbide prepared at 6% partial pressure of  $\text{SiF}_4$ .

Annealing temp. (K)	Total F ( $10^{22}\text{ cm}^{-3}$ )	% bonded to Si	% bonded to C	At. % F	Total F evolved ( $10^{22}\text{ cm}^{-3}$ )	% of F evolved from Si	% of F evolved from C
400	4.16	28.7	71.3	43.1	0	0	0
600	4.05	27.5	72.5	41.9	0.12	72.6	27.4
800	3.85	23.6	76.4	39.9	0.32	91.5	8.5

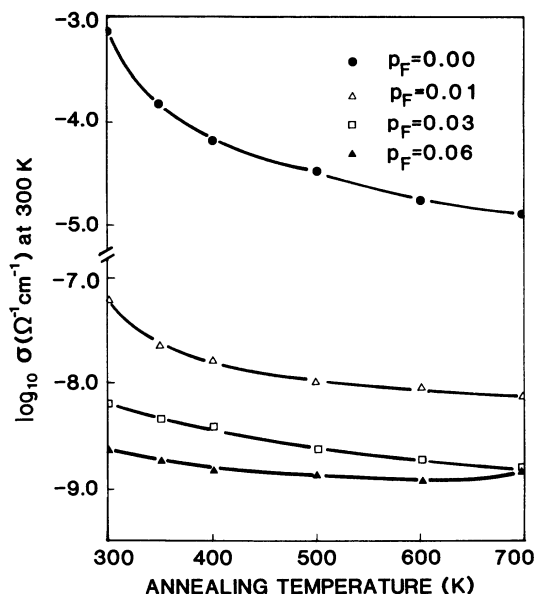


FIG. 6. Room-temperature dark conductivity of samples with different fluorine contents at different annealing temperature.

where  $\omega_1$  is the band-center frequency. The integral is extended over the entire band and is calculated by evaluating the area under the absorption curve, the error in the evaluation being less than 5%. The density of fluorine atoms in films is calculated on the assumption that fluorine atoms which are not bonded to silicon atoms are bonded to carbon atoms. The results are summarized in Table II. Fluorine is found to attach preferentially to carbon over silicon. The quantity representing the preferential fluorine attachment to carbon is defined as

$$\frac{(\text{concentration of C-F bonds}) \times (\text{Si content})}{(\text{concentration of Si-F bonds}) \times (\text{C content})}$$

and is found to have a value between 1.75 and 2.48, the latter being the value at the highest fluorine concentration. Likewise in  $a\text{-Si}_{1-x}\text{Ge}_x\text{:H}$  alloys, Paul *et al.*<sup>17</sup> have found that incorporated hydrogen attached preferentially to Si over Ge atoms.

#### D. Annealing effects

Figures 5(a) and 5(b) show the infrared-absorption bands of Si-F and C-F stretching modes, respectively, in  $a\text{-SiC:F}$  ( $p_F=0.06$ ) at three different annealing temperatures. The annealing at 400, 600, and 800 K

were carried out in argon atmosphere for 1 h each. The bonded fluorine concentration changes by  $\sim 7\%$  when annealed up to 800 K. Fluorine is observed to evolve mainly from silicon. The atomic percentage of fluorine bonded to carbon, in fact, increases at higher annealing temperatures. This may be due to the trapping of fluorine atoms evolved from silicon by carbon atoms. Results are summarized in Table III. We speculate that the appetite of silicon and carbon for fluorine atoms goes through a maxima at different bonded fluorine concentrations and at different  $p_F$ . Hence the preferentiality factor at different fluorine levels and at different annealing temperatures will be different. Even at 800 K the fluorinated amorphous silicon carbide holds on to  $\sim 93\%$  of its bonded fluorine atoms and thus satisfies most of its dangling bonds. The inference is also confirmed by the variation of dark conductivity at room temperature with annealing as shown in Fig. 6. No deterioration of the electrical conductivity of the film due to evolution of fluorine is observed even at highest annealing temperature.

#### IV. CONCLUSIONS

An unexpectedly high total fluorine atomic concentration, much more than needed to satisfy broken bonds, is found in the amorphous films. As the partial pressure of  $\text{SiF}_4$  in the sputtering atmosphere is changed from 1.0 to 6.0%, the fluorine concentration varied from 8 to 43 at.%. It is worthwhile to point out that  $\text{SiC:H}$  samples sputtered in 45% partial pressure of hydrogen have shown<sup>18</sup> to contain atomic density of hydrogen as high as 100% relative to (Si + C). The density of amorphous alloys decreased with increasing fluorine composition. The fluorinated samples did not show any deterioration up to the annealing temperature of 800 K. The bulk of fluorine that evolved on annealing was from silicon.

#### ACKNOWLEDGMENTS

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- <sup>1</sup>E. A. Fagen, in *Amorphous and Liquid Semiconductors*, edited by J. Stuke and W. Brenig (Taylor and Francis, London, 1974), pp. 601–607.
- <sup>2</sup>K. Nair and S. S. Mitra, *J. Non-Cryst. Solids* 24, 1 (1977).
- <sup>3</sup>T. Shimada, Y. Katayama, and K. F. Komatsubara, *J. Appl. Phys.* 50, 5530 (1979).
- <sup>4</sup>H. Wieder, M. Cardona, and C. R. Guarnievi, *Phys. Status Solidi B* 92, 99 (1979).
- <sup>5</sup>R. Dutta, P. K. Banerjee, and S. S. Mitra, *Solid State Commun.* 42, 219 (1982).
- <sup>6</sup>A. Madan, S. R. Ovshinsky, and E. Benn, *Philos. Mag. B* 40, 259 (1979).
- <sup>7</sup>H. Matsumura, Y. Nakagome, and S. Furukawa, *Appl. Phys. Lett.* 36, 439 (1980).
- <sup>8</sup>W. Y. Ching, *J. Non-Cryst. Solids* 35-36, 61 (1980).
- <sup>9</sup>J. Goubeau, F. Haenschke, and A. Ruoff, *Z. Anorg. Allg. Chem.* 366, 113 (1969).
- <sup>10</sup>I. McAlpine and H. Sutcliffe, *Spectrochim. Acta* 25, 1723 (1969).
- <sup>11</sup>G. Herzberg, *Molecular Spectra and Molecular Structure* (Van Nostrand, New York, 1954), p. 195.
- <sup>12</sup>E. B. Wilson, J. C. Decius, and P. C. Cross, *Molecular Vibrations* (McGraw-Hill, New York, 1955), p. 166.
- <sup>13</sup>P. N. Schatz and D. F. Hornig, *J. Chem. Phys.* 21, 1516 (1953).
- <sup>14</sup>L. Genzel and T. P. Martin, *Surf. Sci.* 34, 33 (1973).
- <sup>15</sup>M. H. Brodsky, M. Cardona, and J. J. Cuomo, *Phys. Rev. B* 16, 3556 (1977).
- <sup>16</sup>J. Hofman, J. Lely, and J. Volger, *Physica (Utrecht)* 23, 236 (1957).
- <sup>17</sup>W. Paul, D. K. Paul, B. Von Roedern, J. Blake, and S. Oguz, *Phys. Rev. Lett.* 46, 1016 (1981).
- <sup>18</sup>R. Dutta, P. K. Banerjee, and S. S. Mitra, *Phys. Status Solidi B* 113, 277 (1982).