Determination of oscillator strength of C–F vibrations in fluorinated amorphous-carbon films by infrared spectroscopy

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Fluorinated amorphous-carbon (a-CF_x) films deposited by plasma-enhanced chemical-vapor deposition were investigated by Fourier transform infrared transmission spectroscopy and Rutherford backscattering. The proportionality constant between the fluorine concentration and the integrated absorption of C–F vibration modes is $3.52\pm0.3\times10^{19}\,\mathrm{cm}^{-2}$, and is constant within experimental uncertainty over a wide range of processing conditions. It is shown that the fluorine content can be accurately determined from the infrared absorption spectrum of a-CF_x films.
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The demand for improvements in the switching performance of ultra-large-scale-integration devices has lead to an increased need for low-dielectric-constant materials that can reduce delay in the switching performance due to the parasitic capacitance of multilevel interconnections. As a promising material for interlayer dielectric application, a-CF_x deposited by plasma-enhanced chemical-vapor deposition (PECVD) has attracted considerable attention and has been actively studied due to its low dielectric constant, excellent mechanical properties, and gap fill capability.[1] This material has an amorphous C–C cross-linked structure and has C–F bonds like those in polytetrafluoroethylene. The C–C cross-linked structure contributes to the film's thermal stability. The strong C–F bonds decrease its dielectric constant. It is important to determine and control the fluorine concentration of a-CF_x films for interlayer dielectric application.

In this work, we report on the Fourier transform infrared (FTIR) transmission studies of a-CF_x films prepared under different deposition conditions. The fluorine atomic densities in the films, as measured by Rutherford backscattering spectroscopy (RBS), were compared with the IR absorption intensities of the C–F vibration bonds in the range of 1000–1400 cm^{-1} to determine the oscillator strength for these bonds applying the Lambert–Beer law. We empirically found that it is a valid way to determine the fluorine content in the films by the quantitative analysis of FTIR data.

a-CF_x films were prepared in a conventional capacitively coupled, 13.5 MHz rf PECVD system (base pressure around 10^{-7} Torr). The films were deposited on substrates mounted on the anode. The polished p-type single-crystalline silicon (100) was used as the substrate material, and C_2H_2 and CF_4 gas mixtures were used as feed gases. The substrate temperature was varied from 323 to 753 K. Temperature was calibrated by placing a thermocouple to a silicon sample, which was attached to the anode by a stainless-steel holder. The thickness of the films was obtained from profilometer measurements. During the deposition process, the total pressure and rf power were kept constant, while the deposition temperature and gas flow ratios [$\mathrm{GFR}=CF_4/(CF_4+C_2H_2)$] were the variable process parameters. Table I lists the deposition parameters and film properties for the a-CF_x films used in this letter.

The composition of the films and atomic densities were measured by Rutherford backscattering using a 2.3 MeV He^{++}-ion beam. Experimental data were collected in the normal exit detector mounted at 170°, and the Rutherford backscattering cross section was used to evaluate the data. The hydrogen forward scattering (HFS) detector was calibrated using a CH_2 standard sample, and 3% absolute error for fluorine concentration was obtained by several measurements of samples with known fluorine contents. FTIR transmission spectra were recorded with a Perkin–Elmer spectrometer with 8 cm^{-1} resolution. The transmission spectra of the a-CF_x films were obtained by subtracting the spectrum of the silicon substrate from the spectrum of the silicon substrate with a-CF_x film.

Figure 1 shows a representative IR transmission spectrum $T(\omega)$ of the a-CF_x films. The transmission spectra were recorded in the range of 400–4000 cm^{-1}. The refractive index of the a-CF_x films is intermediate between that of the silicon substrate and air. This index mismatch at the film–substrate interface leads to broad, shallow interference fringes in the IR transmission spectra, as shown in Fig. 1. The C–F absorption bands are superimposed on these fringes. Since the strongest C–F bands were present in the 1000–1400 cm^{-1} region, our investigation was focused on this range. The quantitative analysis of the IR results is based on Beer's law: the concentration of the bonds contributing to an IR-active band (N) is proportional to the integrated absorption of the band. It can be described using the following equation:

$$N=A\int\frac{\alpha(\omega)}{\omega}d\omega=AI. \tag{1}$$

In atomic percent, the above equation can be expressed as

$$N\%=\frac{A}{\rho}\int\frac{\alpha(\omega)}{\omega}d\omega=\frac{A}{\rho}I, \tag{2}$$

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TABLE I. Deposition parameters and film properties of the a-CF_x films used in this letter.

Sample No.	Gas flow ratio	Pressure (mTorr)	Temperature (K)	Power (W)	Thickness (μm)	Integrated absorption I (cm^{-1})	F%	C%	H%
1	0.700	500	673	50	2.2	128.7	0.07	0.54	0.36
2	0.800	500	673	50	1.3	323.5	0.17	0.61	0.22
3	0.850	500	673	50	1.4	502.9	0.20	0.55	0.25
4	0.875	500	673	50	1.0	660.3	0.29	0.60	0.11
5	0.883	500	673	50	0.9	687.9	0.32	0.60	0.08
6	0.892	500	673	50	0.8	690.7	0.32	0.59	0.09
7	0.883	500	323	50	1.4	988.2	0.50	0.47	0.03
8	0.883	500	518	50	1.0	980.6	0.49	0.47	0.04
9	0.883	500	593	50	1.2	724.6	0.37	0.57	0.06
10	0.883	500	663	50	1.2	634.5	0.28	0.55	0.16
11	0.883	500	703	50	1.0	621.6	0.26	0.66	0.07

where A is a proportionality constant which varies as the inverse of the oscillator strength, $\alpha(\omega)$ is the frequency-dependent absorption coefficient, ω is the frequency in cm^{-1}, I is the integrated absorption, and ρ is the atomic density of a-CF_x films. Atomic density ρ is obtained as a ratio of surface atomic density directly from RBS measurements to the thickness obtained from profilometer measurements. $\alpha(\omega)$ is determined from the film thickness and IR transmission spectra. The integration is performed from 1000 to 1400 cm^{-1}, the absorption band that contains the five individual C–F bands.

Based on Beer's law, several investigations have been conducted on the quantitative analysis of hydrogen in hydrogenated amorphous-silicon (a-Si:H) film.[2–4] Brodsky, Cardona, and Cuomo[2] investigated silicon–hydrogen bonds in a-Si:H films and showed that IR transmission can be used as a valid method to determine the hydrogen content. However, it was shown by Langford, Fleet, and Nelson[3] that the method of Brodsky, Cardona, and Cuomo, although in principal correct, could lead to errors of the order of 75% in the quantitative analysis. These errors were mainly attributed to the occurrence of coherent multiple reflections in the thin film, which lead to an increase of the effective optical path length. For films with thicknesses of less than 1 μm, Maley and Szafranek[4] showed that Brodsky's method can lead to significant errors in determining absorption coefficients. By using thicker films, the influence of these errors can be reduced significantly.

In the present study, the absorption spectrum $\alpha(\omega)$ is determined using the Lambert–Beer law $\alpha(\omega) = \ln[T_0(\omega)/T(\omega)]/d$, where d is the a-CF_x film thickness and $T_0(\omega)$ is the fitted base line corresponding to zero absorption, as indicated by the dotted line in Fig. 1. A polynomial function with six coefficients was used to fit the base line. In order to eliminate the effect of the error sources mentioned above, thick a-CF_x films with the thicknesses in the range of 0.8–2.1 μm were used for FTIR transmission measurements. We found that the samples, with different thicknesses prepared under the same experimental conditions, have integrated absorption intensity variations within the experimental uncertainty. But, great care has to be taken if this method is applied to thinner films.

We have shown before[5] that strong absorption in 1000–1900 cm^{-1} region consists of ten peaks from carbon–fluorine, carbon–carbon, and carbon–oxygen vibration modes. In order to obtain the total integrated absorption of the five C–F bands, we fitted the IR absorption spectra from 1000 to 1500 cm^{-1} with seven peaks (five peaks from C–F vibration modes and two peaks from C–C vibration modes). The sum of the integrated absorption of the five C–F bands was used as the total integrated absorption from C–F vibration modes. Figure 2 presents the total integrated absorption

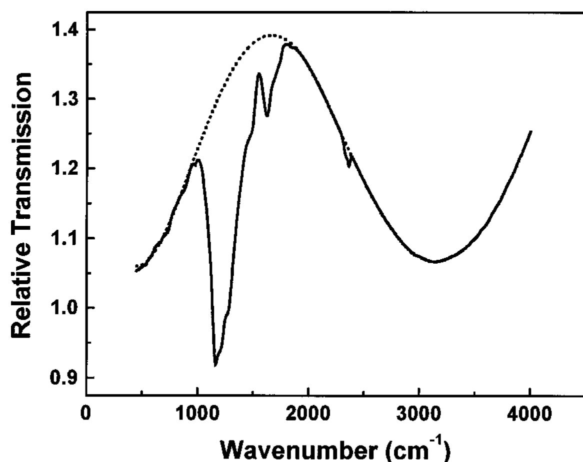

FIG. 1. IR transmission spectrum of the a-CF_x films. The solid line is the experimental spectrum. The dotted line is the fitted base line.

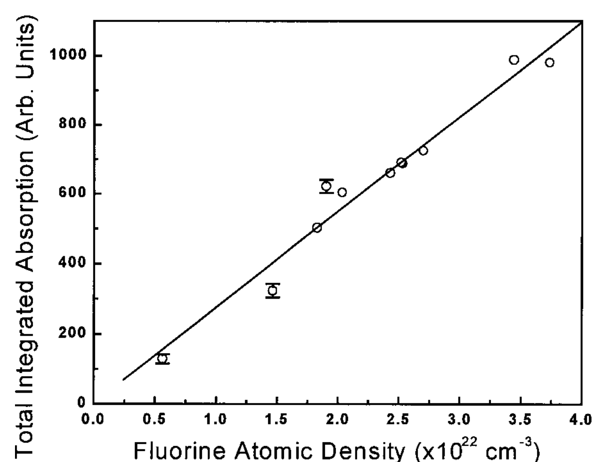

FIG. 2. Total integrated absorption of C–F bands in the 1000–1400 cm^{-1} region is plotted as a function of the fluorine atomic density in the films.

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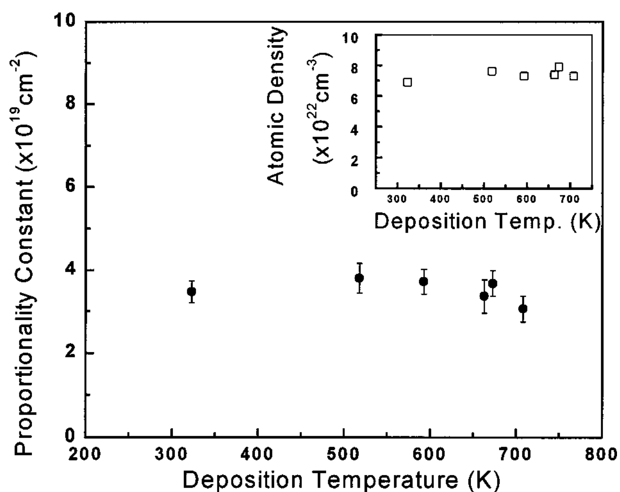

FIG. 3. Proportionality constant A of the a-CF_x films is plotted as function of the deposition temperature, with constant GFR = 0.883. The atomic density of the a-CF_x films is also plotted as a function of deposition temperature as an inset. Error for the atomic density measurements is constant at 3.3%.

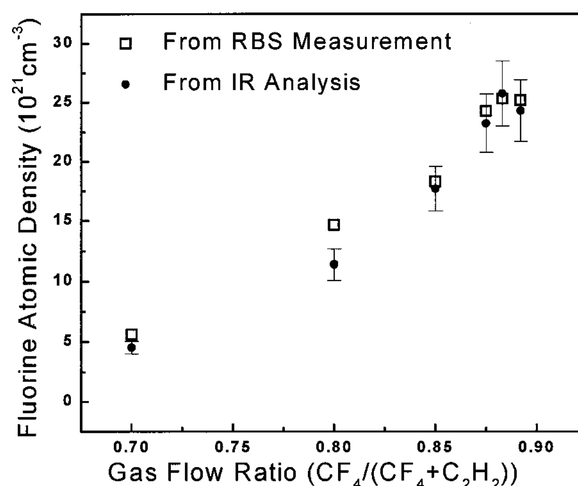

FIG. 4. Plot of fluorine content determined by analysis of IR data and RBS measurement as a function of GFR. In the experiment, the deposition temperature is kept constant at 673 K. The fluorine concentration obtained from RBS measurements has a 3% error.

of five C–F bands as a function of the fluorine concentration for all the films described in Table I. Error was calculated based on the standard deviation of at least five Gaussian fits of the IR data with different starting peak positions each time. Error bars are indicated for values above 2%. The total integrated absorption intensity of these bands increases linearly with an increase in the fluorine content. This clearly indicates that there is no significant variation in the oscillator strength of these bands. Obviously, this simplifies the problem. We can compare the fluorine atomic density with the total integrated absorption intensities of five C–F bands to obtain the average proportionality constant A for C–F bands. With this proportionality constant, the fluorine concentration can be accurately determined simply by integrating IR absorption of C–F bands for the films prepared under the conditions comparable to the ones used in this letter.

Following the above procedure, we calculated proportionality constant A for a-CF_x films deposited using a C_2H_2 and CF_4 gas mixture at different deposition temperatures. Figure 3 shows the plot of proportionality constant A versus deposition temperature. The atomic density of a-CF_x films, determined from RBS and thickness measurements, is shown in the inset of Fig. 3 as a function of deposition temperature. Within experimental uncertainty, proportionality constant A and atomic density are constant and the their values are about $(3.52\pm0.3)\times10^{19}\,\mathrm{cm}^{-2}$ and $(7.40\pm0.3)\times10^{22}\,\mathrm{cm}^{-3}$, respectively. Error in the calculations arises from the error in N, atomic density, and in the integration of absorption, according to Eq. (2). Our previous results[5] have shown that the films prepared at room temperature consisted mainly of $-CF_2$ chains. An increase in the deposition temperature can increase the degree of cross linking between $-CF_2$ chains, and hence, lead to a cross-linked network structure. A constant value of the proportionality constant, and hence, the integral oscillator strength for the five C–F bonds in the films deposited over a large temperature range, indicates that there is no significant dependence of the oscillator strength on the structure of a-CF_x films. This is different from a-C:H films. For a-C:H films, some studies have shown that the oscillator strength is dependent on the film structure.[6]

Using $(3.52\pm0.3)\times10^{19}\,\mathrm{cm}^{-2}$ as the proportionality constant A, we determine the fluorine content in a distinct set of a-CF_x films deposited at 673 K with different GFR values. Figure 4 shows the plot of fluorine atomic density obtained from the analysis of IR spectra, as well as from RBS measurements, as a function of GFR. It is clear from Fig. 4 that the value of fluorine content from IR data is in excellent agreement with RBS measurements. This indicates that fluorine concentration in a-CF_x films can be accurately determined using the procedure described in this letter. The largest component of error in this calculation is from the calculation of the proportionality constant from Fig. 3. Thus, the error is the sum of the error in Fig. 3 plus the error in calculation of integrated absorption I.

It should be mentioned that the constant integral oscillator strength is appropriate for the films deposited at the temperature below 703 K. When the deposition temperature is above 703 K, a-CF_x films exhibit lower oscillator strength. Increase in the sp^2 hybridized graphitic state may lead to lower oscillator strength when the films are deposited above 703 K.

In summary, FTIR and RBS were used to characterize fluorinated amorphous-carbon films deposited by PECVD. The proportionality constant A was found to be constant within experimental uncertainty for the samples prepared under certain experimental conditions. We used this integral oscillator strength to determine accurately the fluorine concentration of a-CF_x films deposited at 703 K with variable GFR. This indicates that it is a valid method to determine fluorine content in a-CF_x films by analysis of IR spectra.

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