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I.r. spectra resolution in fluorinated silicon nitride films

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The broad i.r. Si–N band (700–1200 cm^{-1}) in fluorinated silicon nitride films has been resolved. I.r. spectra of the samples have been fitted using Gaussian curves centred in positions determined from the maxima of the negative second derivative of the digitized spectra. In silicon nitride films deposited by plasma-assisted chemical vapour deposition from SiH_4–NF_3–NH_3–N_2 gas mixtures, –SiF_n radicals ($n = 1$–3) incorporated in their structures have been detected. The relative concentrations of the different fluorine radicals present in the network depend on the NF_3 flow ratio used. As the flow ratio increases above 0.5, –SiF and –SiF_2 concentrations in the film reach the steady state. However, an appreciable increase in –SiF_3 and [–SiF_2–]$_n$ concentrations has been observed.

1. Introduction

Plasma silicon nitride films are widely used for the final passivation layer and insulation in microelectronic devices. Conventional plasma silicon nitride films deposited from silane and ammonia gas mixtures present a high degree of hydrogen incorporation into their network. Several attempts have been made to avoid the unwanted effects of hydrogen presence by using different halogen gas mixtures [1–4].

Fluorinated silicon nitride films deposited from a reactive plasma of SiH_4–NF_3–NH_3–N_2 exhibit a higher thermal stability than that of the conventional hydrogenated silicon nitride films deposited from SiH_4–NH_3–N_2 gas mixtures [5, 6]. The fluorine content in the films increases when the fluorinated species concentration in the reactive plasma becomes higher. The film properties are strongly influenced by the fluorine atoms present in the network. The mechanism of fluorine incorporation is not well known.

Typical fluorinated silicon nitride films show a broad band attributed to Si–N stretching vibration in their i.r. spectra. As mentioned in a previous paper [7], a continuous shift in the Si–N band towards high frequencies was observed when the fluorine content in the gas mixture was increased. The broadening and shift of the Si–N band were explained by the presence of fluorine atoms incorporated in the network, but the different contributions to the i.r. absorption band have not been established yet.

In this paper, a general method of resolving overlapping spectra has been used [8, 9]. This method is applied to the i.r. absorption band (700–1200 cm^{-1}) in fluorinated silicon nitride films. The positions of the different peaks included in the broad absorption band were obtained from the maxima of the negative derivative of the measured i.r. spectra. In this way, an adequate assignation of peaks leads to separate different chemical bonding states of fluorine in the fluorinated silicon nitride films.

As a practical application, the i.r. spectra corresponding to fluorinated silicon nitride films obtained from SiH_4–NF_3–NH_3–N_2 with increasing fluorine content have been resolved. From these results, the proportion of –SiF_n ($n = 1$–3) radicals in the silicon nitride network has been found to be dependent on the total fluorine content.

2. Experimental procedure

Silicon nitride films were deposited on silicon substrata in a commercial Plasmatherm, planar reactor, at a constant pressure (700 mTorr), temperature (350 °C), r.f. power (0.28 W cm^{-2}) and total flow rate (500 sccm) using SiH_4–NF_3–NH_3–N_2 gas mixtures. The samples were obtained with an $[NF_3]/([NH_3] + [NF_3])$ flow ratio within the range 0–1, keeping the $[NH_3] + [NF_3]$ and the $[SiH_4]$ flows constant at 10 sccm.

The measurement of the i.r. spectra was carried out in a Hitachi spectrophotometer, model 270-50. For this purpose, the samples were deposited on to (1 1 1) p-Si substrates, polished on both sides. Every experimental spectrum was digitized (256 points) in the range 400–1600 cm^{-1} with an HP-85 computer.

3. Mathematical procedure

As mentioned above, the positions of the i.r. bands were determined from the maxima of the negative second derivative of the digitized spectra in the range 400–1600 cm^{-1}. This procedure has proved to be very useful to detect features in other methods such as Auger electron spectroscopy and electron energy-loss spectroscopy [8]. In this way the maxima in the

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negative second derivative correspond to the maxima in the original spectra [8]. However, in order to avoid non-real features which can appear in the negative second derivative as a consequence of the loss of signal-to-noise ratio, the original i.r. spectra have been used to corroborate the observed peaks in the negative second derivative.

Different methods have been proposed to calculate the second derivative and also to smooth the results to improve the signal-to-noise ratio. The calculation of smoothed derivatives with the method described by Savitzky and Golay [10] is one of the most popular methods. However, the indiscriminated use of least-squares polynomial smoothing (Savitzky and Golay methods) may produce some undesirable effects such as a shift of the peak positions [11] which limits its use in some applications. Other methods of smoothing data such as the binomial smoothing filter or Fourier transform of the spectra [11] do not present this problem and therefore they are more appropriate for the present work. In fact it has been confirmed that the two last methods lead to the same band positions. In the present work, Fourier transform methods were used. They allow one to calculate the second derivative and smoothing of data simultaneously.

The algorithm is as follows. From the point of view of filter theory [12, 13] the smoothing process is given by the equation

$$s_f(t) = s_i(t) * v(t) \quad (1)$$

where $s_f(t)$ represents the signal, spectrum etc. after smoothing, $s_i(t)$ is the input signal (i.e. the digitized i.r. spectrum in the present work) and $v(t)$ is the low-pass filter which attenuates the high-frequency components of the input signal. Here the symbol * represents convolution. The application of the convolution theorem to Equation 1 leads to the equation

$$S_f(f) = S_i(f)V(f) \quad (2)$$

Capital letters indicate the Fourier transform of the respective symbols of Equation 1. In addition, there is an equation relating the second derivative of a function and its Fourier transform,

$$\frac{d^2 s_i(t)}{df^2} \Longleftrightarrow -4\pi^2 f^2 S_i(f) \quad (3)$$

where the symbol $\Longleftrightarrow$ stands for the Fourier transform [14]. Therefore the evaluation of the second derivative of a function $s_i(t)$ can be carried out by applying Equations 3 and 2, and evaluating the inverse Fourier transform of the function obtained.

The Blackman D4 filter [12] has been chosen in this work because its high performance makes this filter very suitable in spectroscopic applications [15]. In addition to the above algorithm, fast Fourier transform (FFT) methods were used in order to spend as short a computer time as possible [14].

Once the band positions were determined by the method described above, the contributions of the different bands to the measured spectra were calculated by means of non-linear regression methods in order to obtain quantitative results. The individual bands were considered to be Gaussian functions and the measured spectra were considered to be a combination of Gaussian functions [9]. The peak height and the Gaussian width were used as fitting parameters to fulfill the least-squares criterion between the experimental and simulated spectra.

4. Results and discussion

Fig. 1 shows the i.r. spectra of the fluorinated silicon nitride films in the 400–4000 cm^{-1} range for different $[NF_3]/([NH_3] + [NF_3])$ flow ratios (0–1). The shift and broadening of the Si–N band has currently been explained by fluorine incorporation into the silicon nitride network [7, 16]. However, no identification of the i.r. features of such a band has been given until now. In fluorinated amorphous silicon films, the i.r. peaks around 810–1030 cm^{-1} have been attributed to $-SiF_n$ radicals ($n = 1$–4) [17, 18]. Therefore, the changes observed in the Si–N band (Fig. 1) could be attributed to the above-mentioned radicals incorporated in the silicon nitride film. In order to resolve the broad Si–N band in the 400–1600 cm^{-1} range, the negative second derivatives of the i.r. spectra of Fig. 1 ($-N''$) have been calculated and the results are given in Fig. 2. The positions of the maxima of i.r. spectra are given in Table I.

The peak at 610 cm^{-1} (A) corresponds to the network vibration of the silicon substratum. In the i.r. spectra (Fig. 1) this peak appears isolated and we have used it as a reference point.

The peaks in Table I, excluding the peak at 610 cm^{-1}, overlap in the 700–1200 cm^{-1} range. The peak at 1220 cm^{-1} (H) has been attributed to N–H bond vibration [19], and its intensity in $-N''$ curves (Fig. 2) increases with the $[NF_3]/([NH_3] + [NF_3])$ flow ratio. This behaviour is related to the increase in the N–H concentration as reported elsewhere [7].

In Fig. 2, the spectrum labelled 0 corresponds to the silicon nitride film without fluorine atoms in its network. In the 700–1200 cm^{-1} range, the spectrum only displays one peak at 830 cm^{-1} (C in Table I) which has been assigned to the Si–N stretching band. No appreciable change has been detected in the Si–N peak for the studied samples.

The B, D, E, F and G peaks, which increase with the fluorine content, are probably due to fluorine bonding. The fluorine atoms are mainly or entirely bonded to silicon in fluorinated silicon nitride films deposited from SiH_4–NF_3–NH_3–N_2 gas mixtures [2, 5]. In our samples various bonding configurations of fluorine to silicon ($-SiF_n$, $n = 1$–4) can be expected, according to the results obtained by Shimada and Katayama [17] and Fang *et al.* [18] for amorphous silicon. The force constant of the Si–F bond mainly changes by induction effects of the substituting groups. The progressive increase of fluorine atoms in the $-SiF_n$ radicals (from 1 to 4) must produce a shift towards high values in the Si–F stretching vibration frequency. Therefore, the features at 859, 920–966 and 1073 cm^{-1} should be assigned to the stretching modes of the $-SiF_n$ radicals, with $n = 1$, 2 and 3 respectively, in agreement with Shimada and Katayama [17] and Fang *et al.* [18].

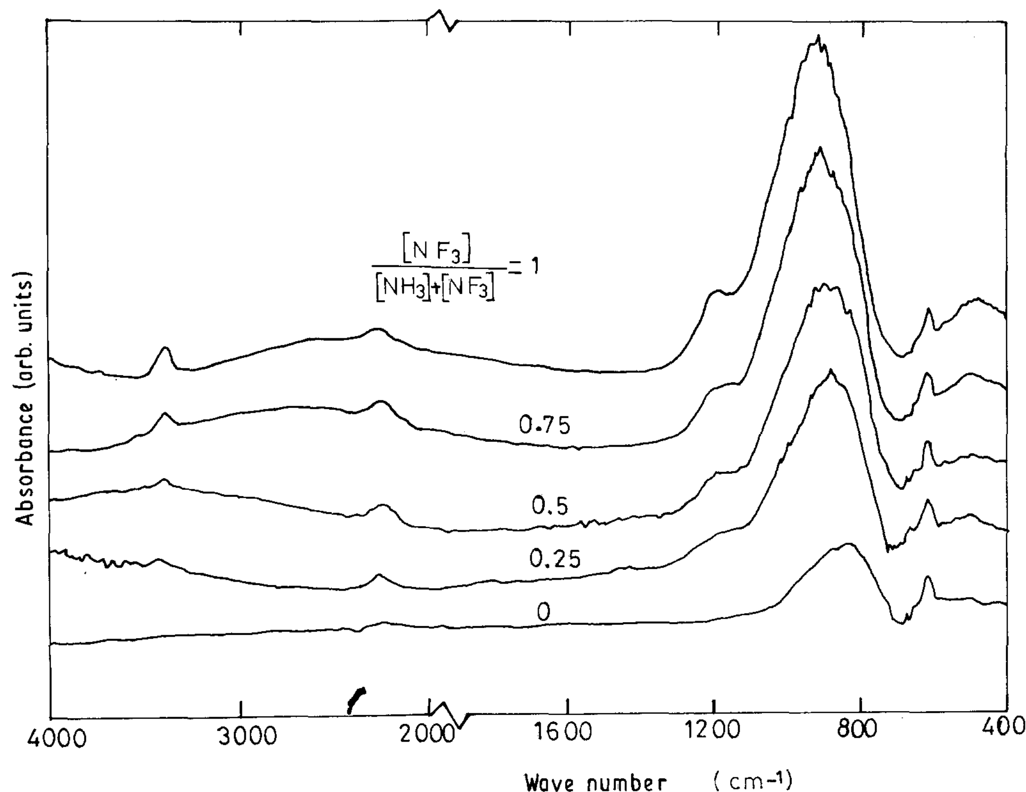

Figure 1 I.r. spectra of fluorinated silicon nitride films in the 400–4000 cm^{-1} range for different $[NF_3]/([NH_3] + [NF_3])$ flow ratios.

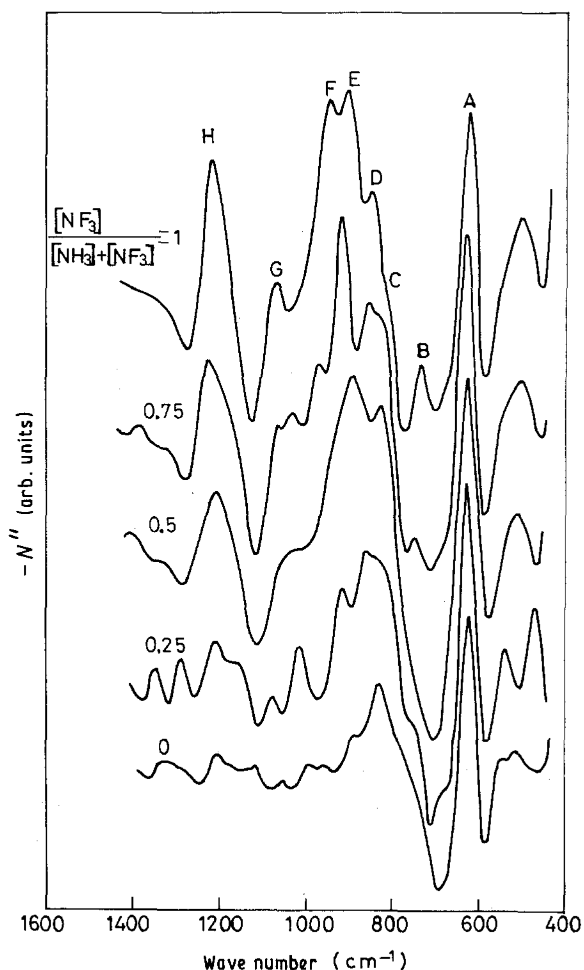

Figure 2 I.r. spectra in the negative second derivative mode ($-N''$), as in Fig. 1.

TABLE I Position of the maxima of i.r. spectra

Peak	Position (cm^{-1})	Assignment
A	610	Si–Si
B	730	$[-SiF_2-]_n$
C	830	Si–N
D	859	Si–F
E	920	$Si-F_2$
F	966	$[-SiF_2-]_n$
G	1073	$Si-F_3$
H	1220	N–H

Khanna *et al.* [20] and Bassler *et al.* [21] showed that the polymer $[-SiF_2-]_n$ presents a band at higher frequency than the $-SiF_2-$ radical, so the peaks at 920 and 966 cm^{-1} can be attributed to $-SiF_2-$ and $[-SiF_2-]_n$, respectively. The peak at 730 cm^{-1} (B), which increases along with the 966 cm^{-1} band, should also be attributed to the polymer according to Khanna *et al.* [20].

Finally, the peak at 1073 cm^{-1} could be assigned either to $-SiF_3$ radicals [17] or SiF_4 molecules trapped in the silicon nitride network [18]. The former interpretation would be supported by the following facts: (a) in our experimental conditions, NF_3 molecules are the unique fluorine source and $-SiF_3$ radicals must be a previous step to the formation of SiF_4 molecules [17]; and (b) the difference between the position of this peak (1073 cm^{-1}) and the reported position for the peak related to $-SiF_3$ radicals at 1010–1030 cm^{-1} [17] could be attributed to the association of $-SiF_3$ radicals.

TABLE II Band area contributions to the i.r. spectra A (arbitrary units)

Band position (cm^{-1})	$[[NF_3]/([NH_3] + [NF_3])]$				
	0	0.25	0.50	0.75	1
1220 (NH)	1.5	6.02	7.52	10.53	15.04
1073 (SiF_3)	–	13.53	18.05	27.07	33.84
966 $[-SiF_2-]_n$	–	24.82	31.58	47.38	65.42
920 (SiF_2)	–	13.16	18.80	24.44	24.44
859 (SiF)	–	13.16	22.56	22.56	22.56
830 (SiN)	29.33	34.21	31.77	31.77	31.77
730 $[-SiF_2-]_n$	–	0.19	0.56	0.75	0.94

In order to evaluate the different contributions of the bands included in the experimental spectra, the IR spectra of Fig. 1 were fitted to a combination of Gaussian functions, as described above, in the range 695–1455 cm^{-1}. In Fig. 3, the experimental results (continuous line) and the fitted curves (broken line) for samples with fluorine atoms incorporated in their network are shown. As can be observed, the agreement between curves is very good. The Gaussian curves area contributing to the spectra are given in Table II. They have been determined from the equation

$$\text{Band area} = \int \text{Abs}(\omega)\, d\omega \qquad (4)$$

where ω = wave number.

It should be pointed out that the Si–N band area does not vary appreciably when NF_3 instead of NH_3 is used as reactant gas. Therefore, the NF_3 flow seems to have no influence on the total number of Si–N bonds. The increase in –NH radicals with fluorine [7] is corroborated by the increase in the band area of the N–H peak observed in Table II.

The higher the relative NF_3 flow in the gas mixture, the higher the band areas corresponding to silicon–fluorine vibrations. The –SiF and –SiF_2 band areas reach a saturation value but $[-SiF_2-]_n$ and –SiF_3 peaks always increase.

Fig. 4 shows the band area of the different –SiF_n radicals (n = 1–3) as a function of the sum of the absorption band areas of all Si–F stretching vibrations normalized to the Si–N band area. The sum of the i.r. absorption bands at 1073 cm^{-1} (–SiF_3), 966 cm^{-1} ($[-SiF_2-]_n$), 920 cm^{-1} (–SiF_2) and 859 cm^{-1} (–SiF) is proportional to the fluorine content in the films [18]. Therefore, the bonding configuration of silicon and fluorine atoms incorporated into the network for different fluorine contents can be determined.

All the samples present –SiF, –SiF_2, $[-SiF_2-]_n$ and –SiF_3 radicals in their structure and fluorine atoms are preferentially joined to silicon as $[-SiF_2-]_n$. For $[NF_3]/([NH_3] + [NF_3])$ ratio = 0.25 (Fig. 4), the number of fluorine atoms incorporated as –SiF, –SiF_2 and –SiF_3 is nearly the same. This behaviour continues, for small variations in the fluorine content, until a saturation of –SiF and –SiF_2 radicals in the films occurs. From this saturation point, an appreciable increase of –SiF_3 and $[-SiF_2-]_n$ radicals in the network has been detected. The high proportion of fluorine atoms as –SiF_3 and $[-SiF_2-]_n$ in films with

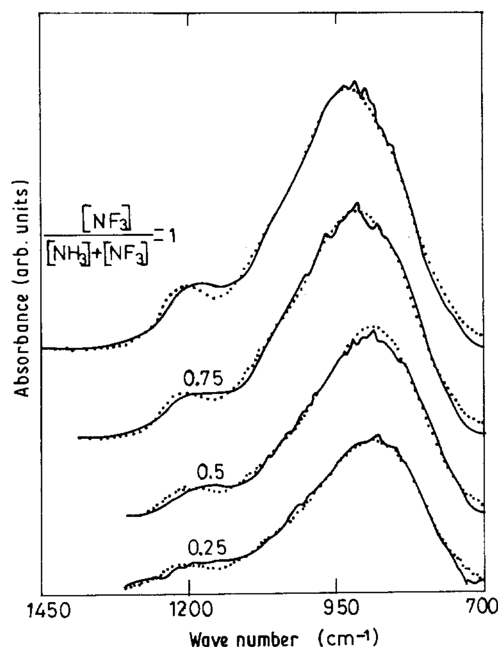

Figure 3 (——) Experimental and (···) fitted i.r. spectra for different $[NF_3]/([NH_3] + [NF_3])$ flow ratios.

$[NF_3]/([NH_3] + [NF_3])$ = 0.75 and 1 could explain their different evolution in moist ambient conditions, pointed out in a previous paper [7]. Alternatively, the presence of radicals (–SiF_3 and $[-SiF_2-]_n$) produce some changes in the structure of the film. In the conditions described, the onset of the degradation process by hydrolysis and/or oxidation is favoured [7]. A more detailed study of the oxidation mechanism of the film is now in progress.

5. Conclusions

A mathematical method, which allows one to resolve overlapped bands, has been applied in this work to i.r. spectra. The broad i.r. band (700–1200 cm^{-1}) in fluorinated silicon nitride films, commonly attributed to Si–N vibration, has been found to be a superposition of five bands. The resolved bands 1073, 966, 920, 859 and 730 cm^{-1} have been assigned to –SiF_3, $[-SiF_2-]_n$, –SiF_2, –SiF and $[-SiF_2-]_n$ vibrations, respectively.

In plasma-fluorinated silicon nitride films deposited from SiH_4–NF_3–NH_3–N_2 gas mixtures, with $[NF_3]/([NH_3] + [NF_3])$ varying from 0 to 1, the proportion of –SiF_n (n = 1–3) radicals in the silicon nitride network has been found to be dependent on

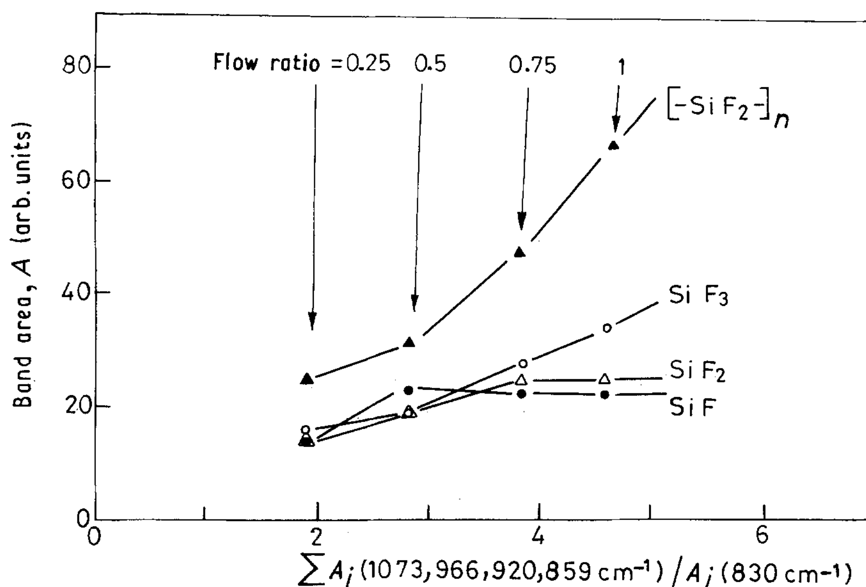

Figure 4 Band area of the different $-SiF_n$ radicals (n = 1–3) as a function of the normalized sum of the absorption band areas of all Si–F stretching vibrations.

the total fluorine. As the total fluorine content increases, the $[-SiF_2-]_n$ and $-SiF_3$ contents increase appreciably. However, the –SiF and $-SiF_2$ radical contents reach a saturation value. In addition, the total number of Si–N bonds in the film is nearly constant.

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