

Si-H Bonding Environment in PECVD α -SiO_xN_y:H Thin Films

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Abstract

We constructed silicon oxynitride thin films of various compositions by Plasma Enhanced Chemical Vapor Deposition and studied the global structure by infrared absorption. The Si-H band frequency is related to the environment of Si atom. We considered the Si-H band as the sum of several gaussian curves corresponding to the different silicon-centered tetrahedra present in the material. The frequency of Si-H bond for each tetrahedron was calculated using Lucovsky linear relations and then the tetrahedra were attributed to gaussians found by decomposition of the band. The results show the presence of tetrahedra with both N and O atoms bound to silicon. These tetrahedra cannot agree with a model of phase separation, however the Random Bonding Model envisages the existence of these environments. So we consider our silicon oxynitride films to be a homogeneous statistical mixture of the various bonds rather than a mixture of phases. Published by Elsevier Science Limited.

1 Introduction

In amorphous silicon compounds the local structure is based on a tetrahedral environment of the silicon. At the present time two models which describe the global structure are proposed:

- a separation in SiO₂, Si₃N₄, Si phases (Random Mixture Model: RMM). In other words this model considers only Si[O₄], Si[N₄], Si[Si₄] tetrahedra.
- a statistical bonds distribution (Random Bonding Model: RBM).^{1–3} In this model, all combinations of atoms around the central

Silicon atom are envisaged. The examination of the bonds in the films by means of Fourier Transform Infrared Analysis can give information about the silicon environment. In particular, the decomposition of the Si-H stretching band allows us to get the near-neighbour atoms of Si-H bonds.

2 Experimental

Films of 600–700 nm thickness were deposited on silicon (100) substrates in a parallel plates PECVD system.⁴ A 440 kHz ASM generator supplied a power of 3 W to sustain the plasma. The pressure was maintained at 20 Pa. No heating was used. The different compositions were obtained by variation of N₂O and NH₃ flows. The SiH₄ flows remained constant for 2 sccm, total flow was maintained at 22 sccm. XPS measurements were performed on a Riber MAC-2 Auger spectrometer. An FTIR Nicolet 4000 spectrometer was used for infrared analysis.

3 Results and discussion

The XPS compositions of five films are presented in Table 1. Flow ratio ($R = F_{\text{NH}_3} / (F_{\text{NH}_3} + F_{\text{N}_2\text{O}})$), increases from 0 to 1. More details are given in the previous paper.^{4–6}

The SiO₂:H IR spectra are characterized by three Si-O bands: 1051 cm⁻¹ (stretching), 822 cm⁻¹ (bending), 441 cm⁻¹ (rocking). A very weak absorption at 2260 cm⁻¹ is related to Si-H stretching vibration, and a band at 3380 cm⁻¹ is attributed to SiO-H.⁷ SiN:H IR spectra present the absorption bands of Si-N stretching, Si-H stretching, SiN-H

Table 1. XPS composition of the films $R = F_{\text{NH}_3} / (F_{\text{NH}_3} + F_{\text{N}_2\text{O}})$

Sample	R	Si	O	N	H
1	0.0	0.29	0.62	0.01	0.08
2	0.4	0.30	0.48	0.08	0.13
3	0.6	0.31	0.32	0.19	0.18
4	0.8	0.34	0.18	0.27	0.21
5	1.0	0.34	0.04	0.35	0.27

stretching and NH bending at 849, 2170, 3340 and 1170 cm^{-1} , respectively⁸ For silicon oxynitride compounds, a continuous evolution of the Si-(O,N) and Si-H bands to the lower frequencies is observed when the N proportion increases. In Fig. 1, the frequency variation of these bands is reported: when $0 < R < 0.4$ the decrease of the wavenumber is weak, but when $0.4 < R < 1$ the slope of the variation is accentuated to the low wavenumbers. This agrees well with composition variation. In Fig. 2, the hydrogen content of films is estimated using the Lanford and Rand method.⁹ The NH and OH contents remain constant for all the samples ($\sim 9 \times 10^{21}$ at cm^{-3}), whereas for $R > 0.6$ silicon-bonded hydrogen increases from 0.5×10^{21} to 22×10^{21} at cm^{-3} .

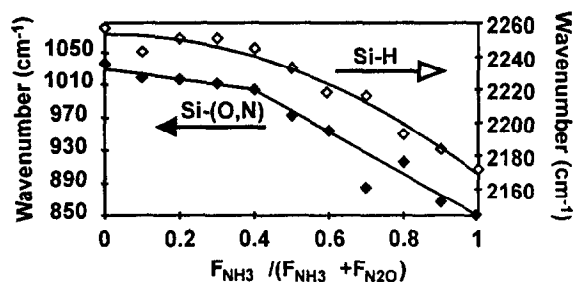
The frequency variation of the Si-H band is due to the variation of silicon near-neighbour atoms. The decomposition of Si-H band in several gaussian components can give us the various silicon environments.

Lucovsky *et al.* showed a linear relation between Si-H vibration frequency and the electronegativity of the other silicon substituting groups.^{10,11} They used the Sanderson stability ratio, which is defined for an atom X by eqn (1) and for a group $R = X_a Y_b$ by eqn (2):

$$SR = \frac{\sqrt{\chi_{\text{Pauling}}(X) - 0.77}}{0.21} \quad (1)$$

where χ is the electronegativity.

$$SR(R) = [(SR(X))^a (SR(Y))^b]^{1/a+b} \quad (2)$$

**Fig. 1.** Evolution of Si-(OnN) and Si-H band vibrations with composition of gas phase.

The linear relations found for SiH, SiH₂, and SiH₃ are:

$$Si - Hv^{(1)} = 1740.7 + 34.7 \sum_{j=1}^3 SR(R^j) \quad (3)$$

$$SiH_2v^{(2)} = 1956.3 + 25.4 \sum_{j=1}^2 SR(R^j) \quad (4)$$

$$SiH_3v^{(3)} = 2086.1 + 22.5SR(R^1) \quad (5)$$

With these relations, several authors used decomposition of the Si-H band to investigate the presence of different tetrahedra.¹²⁻¹⁴ In this work, we took into account tetrahedra like Si(Si_x, O_y, N_z, H) with $x + y + z = 3$, and those having OH, NH, and NH₂ groups (because of the absorption band between 3340 and 3380 cm^{-1}). We assumed that the proportions of tetrahedra with more than two H atoms or OH, NH, NH₂ groups were very weak and could be neglected. With these considerations we obtained a group of 34 tetrahedra shown in Table 2 with their calculated frequencies.

The proximity and the uncertainty of the different frequencies do not allow a decomposition into 34 gaussian curves. In the absence of any data in literature, we used a fixed full-width at half maximum (FWHM) of 60 cm^{-1} , which is the FWHM of Si-H band in SiO₂:H (sample 1). Taking into account the FWHM of the experimental bands, we chose to use a maximum of six gaussians, equally spaced for the automatic fitting (20 cm^{-1} , except for sample 5 where a 40 cm^{-1} spacing was used). In the oxynitride compounds, it is necessary to consider a sufficient number of gaussian because of the large number of possible tetrahedra. We used the criteria $\Delta v < 1$ to establish the correlation between tetrahedron and gaussian:

$$\Delta v = \left| \frac{v_{\text{tet}} - v_{\text{gauss}}^*}{v_{\text{tet}}} \right| \times 100 < 1 \quad (6)$$

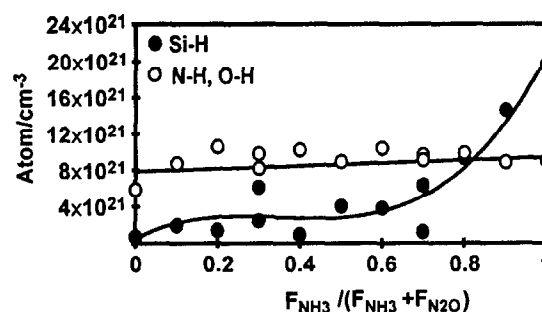
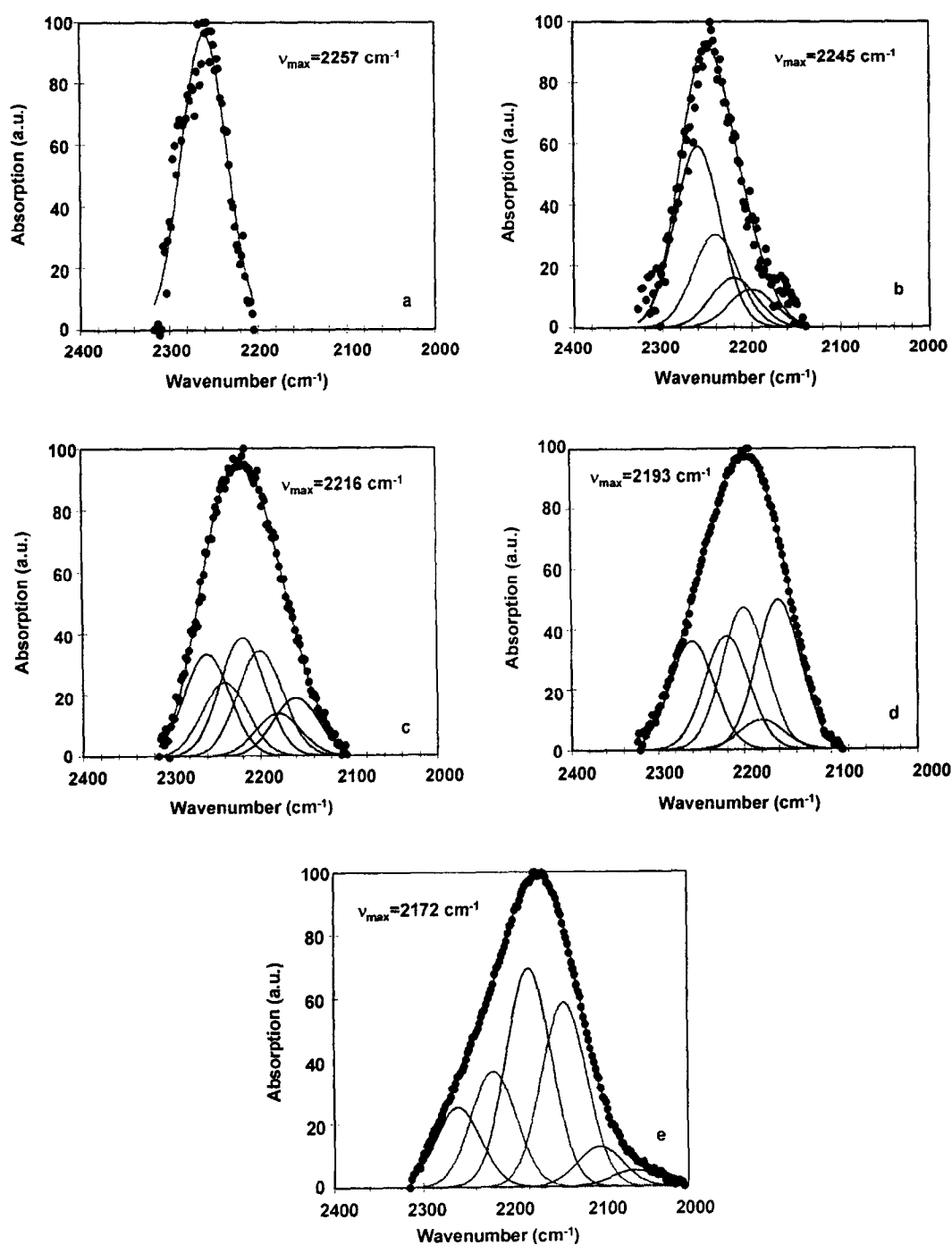
**Fig. 2.** Evolution of H content with gas phase composition.

Table 2. Tetraedra taken into account and their calculated frequency

Tetraedron	$\nu_{tet}(cm^{-1})$	Tetraedron	$\nu_{tet}(cm^{-1})$	Tetraedron	$\nu_{tet}(cm^{-1})$
Si[Si ₃ ,H]	2005	Si[Si ₂ O,(NH),H]	2144	Si[O,N,(NH ₂),H]	2209
Si[Si ₂ ,(NH ₂),H]	2051	Si[Si,N ₂ ,H]	2147	Si[O,N,(NH),H]	2215
Si[Si ₂ ,(NH),H]	2057	Si[Si ₂ O,(OH),H]	2151	Si[N ₃ ,H]	2217
Si[Si ₂ ,(OH),H]	2064	Si[Si ₂ O,H ₂]	2156	Si[O ₂ ,H ₂]	2222
Si[Si ₂ ,N,H]	2076	Si[Si ₂ O,N,H]	2163	Si[O,N,(OH),H]	2222
Si[Si ₂ ,H ₂]	2089	Si[Si ₂ O ₂ ,H]	2179	Si[O ₂ ,(NH ₂),H]	2225
Si[Si ₂ O,H]	2092	Si[N ₂ ,(NH ₂),H]	2193	Si[O ₂ ,(NH),H]	2231
Si[Si,N,(NH ₂),H]	2122	Si[N ₂ ,H ₂]	2194	Si[O,N ₂ ,H]	2234
Si[Si,N,(NH),H]	2128	Si[N ₂ ,(NH),H]	2198	Si[O ₂ ,(OH),H]	2238
Si[Si,N,(OH),H]	2135	Si[N ₂ ,(OH),H]	2206	Si[O ₂ ,N,H]	2250
Si[Si ₂ O,(NH ₂),H]	2138	Si[O,N,H ₂]	2208	Si[O ₃ ,H]	2256
Si[Si,N,H ₂]	2141				

**Fig. 3.** Decomposition results of the Si-H stretching band for the 5 samples: a: sample 1; b: sample 2; c: sample 3; d: sample 4; e: sample 5.

The Si-H band decompositions are presented in Fig. 3. In sample 1 (Fig. 3(a)), only one gaussian appears in decomposition of the Si-H absorption band at 2260 cm^{-1} . The near stoichiometry of the composition ($\text{SiO}_2\text{:H}$) of sample 1 explains that we have only one tetrahedron type: $\text{Si}(\text{O}_3, \text{H})$. An enrichment in the amount of silicon causes the appearance of supplementary gaussians related to tetrahedra with Si-Si bonds.

For sample 2 (Fig. 3(b)) three gaussians appear in the decomposition at 2260 , 2240 , and 2220 cm^{-1} . This is a consequence of the increase of N incorporation in the material. As for sample 1, the main gaussian at 2260 cm^{-1} indicates that the $\text{Si}(\text{O}_3, \text{H})$ tetrahedra are the principal environment of Si-H bonds. We attribute the 2240 and 2220 cm^{-1} gaussians principally to the $\text{Si}(\text{O}_2, \text{N}, \text{H})$ and $\text{Si}(\text{O}, \text{N}_2, \text{H})$ tetrahedra. Meanwhile we cannot exclude some contributions of tetrahedra with OH groups.

In sample 3 (Fig. 3(c)) we can use 6 gaussians spaced by 20 cm^{-1} (2260 , 2240 , 2220 , 2200 , 2280 , 2260 cm^{-1}) in decomposition of the Si-H band. Probably a decomposition with less than six gaussians would agree. This multiplication of gaussians indicates various environments, particularly the tetrahedra $\text{Si}(\text{O}_3, \text{H})$, $\text{Si}(\text{O}_2, \text{N}, \text{H})$, $\text{Si}(\text{O}, \text{N}_2, \text{H})$ and $\text{Si}(\text{N}_3, \text{H})$ as well as their derivated tetrahedra with OH, NH, and NH_2 groups. The 2160 cm^{-1} gaussian is probably due to tetrahedra with Si-Si bonds.

In sample 4 (Fig. 3(d)), 5 gaussians appear at 2260 , 2220 , 2200 , 2180 , 2160 cm^{-1} . The oxygenated tetrahedra are related by the gaussian at 2260 cm^{-1} . The three following gaussians are representative of tetrahedra containing N atoms, NH or NH_2 groups. We see an increase of the 2160 cm^{-1} gaussian, i.e. more Si-Si bonds are present in this sample.

For sample 5 (Fig. 3(e)), as we said before, the large band width requires the use of a 40 cm^{-1} step to keep a decomposition of 6 gaussians with 60 cm^{-1} FWHM. We always observe at 2260 cm^{-1} a gaussian relative to oxygenated tetrahedra. The 2 gaussians at 2220 and 2180 cm^{-1} correspond to tetrahedra with N atoms, NH or NH_2 groups. We have a significative contribution of tetrahedra with Si-Si bonds. In particular 2 weak gaussians appear below 2100 cm^{-1} , indicating the presence of more than two Si-Si bonds per tetrahedra.

4 Conclusion

The continuous evolution of the Si-(O, N) band with composition suggests no phase separation.¹⁵ This implies a multiple environment of silicon atoms, i.e. tetrahedra other than $\text{Si}(\text{O}_4)$, $\text{Si}(\text{N}_4)$, $\text{Si}(\text{Si}_4)$ or than $\text{Si}(\text{O}_3, \text{H})$, $\text{Si}(\text{N}_3, \text{H})$, $\text{Si}(\text{Si}_3, \text{H})$ when we have Si-H bonds. The decomposition of the Si-H absorption band shows the presence of these tetrahedra with various atoms (O, N, Si) which bond to the same silicon. Moreover, we did a decomposition of the XPS Si2p band and the results agree well with prevision of Random Bonding Model. So it seems that our PECVD silicon oxynitride films are a homogeneous statistical bond mixture rather a $\text{SiO}_2\text{Si}_3\text{N}_4$, Si phase separation.

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