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Composition-density and Refractive Index Relations in PECVD Silicon Oxynitrides Thin Films

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Abstract

SiO_xN_y thin films have been prepared by the Plasma Enhanced Chemical Vapour Deposition (PECVD). From the information acquired by XPS for the composition, ellipsometry for the refractive index and grazing X-rays reflectometry for the density, it is possible to establish a relation between these three characteristics of the layer from the Bruggeman and Clausius-Mossoti equations. Published by Elsevier Science Limited.

1 Introduction

The Plasma Enhanced Chemical Vapour Deposition (PECVD) technique is known for producing amorphous thin layers with atomic proportions changing with the composition of the gaz feed and containing some percentage of hydrogen. Silicon oxynitrides deposited by this technique have a large potential for using the thin films as antireflective layers, indeed the refractive index of SiO_2 is 1·46 and that of Si_3N_4 is 2·02. Numerous silicon oxynitride thin films have been previously prepared for microelectronics and the electronic properties are well known. It is noted that the refractive indexes of the layers, prepared by PECVD, are always lower than that of the bulk materials. This is related to the important value of the H amount in the layer which is displayed by Fourier Transform Infra Red spectroscopy (FTIR) (absorption band in the 2000–2200 cm^{-1} range corresponding to the Si-H bond).

Our objective is to establish the relation between the refractive index, the density and the composition of the layers synthesized by the PECVD technique. Generally, the properties of an amorphous material can be described by the Effective Medium Theory. Three models are usually applied for the description of the dielectric function of the oxynitride thin films : the models of Bruggeman,[1–3] that of Maxwell-Garnett,[1–4] and the Lorentz-Lorenz, model.[5] However, the results disagree with the Effective Medium Theory.[6,7] This is attributed to the variation of the density and the presence of hydrogen.

We will establish a relation in which the refractive index, the density and the atomic composition have been measured by ellipsometry, X-ray reflectometry and X-ray photoelectron spectroscopy respectively.

2 Thin Layer Preparation and Characterizations

2.1 Sample preparation

Silicon oxynitride thin films have been prepared using the PECVD technique. The reactor is capacitively coupled to a 440 kHz device and previously described.[8] Two flat and circular electrodes (14 cm in diameter) are connected to the generator and the grounded electrode is the substrate holder. No thermal activation is used and the deposition occurs at room temperature. The gases purchased (Electronic grade) are silane (SiH_4), ammonia (NH_3) and nitrogen protoxide (N_2O). The feed gas composition is monitored by massflowmeter and the pressure kept constant (20–25 Pa) with an absolute gauge and a throttle valve. In all experiments the flow is 22 sccm with a flow of silane of 2 sccm and a total flow of (NH_3 + N_2O) of 20 sccm. The sustained plasma power is 3 watt (19·5 mW/cm^{-2}). The oxynitride thin film has been deposited on silicon wafer (orientation (100)) for the different characterizations described in this paper.

Table 1. Oxynitrides thicknesses and densities

Layer	*Thickness (nm) (ellipsometry)*	*Thickness (nm) (reflectometry)*	*Density (theoretical)*	*Density (reflectometry)*
SiN_y:H	114	116	3·2	2·14
SiO_x:H	131	137	2·2	2·45
SiO_xN_y:H	93	92	—	2·49

2.2 Composition determination : XPS measurements

The XPS and AES characterizations have been made in a SIA-200 Riber UHV chamber with the X-ray of AlK_α (1486·6 eV) filtered with a 100 μm aluminium foil. The energy of the beam is 12 keV. Before all the analyses, an ionic bombardment of Ar^+ is used with an energy of 4 keV. The composition of the layer is calculated from the ratio of the core level areas, taking into account the sensibility coefficient. The composition is given with an error of about 2%. Figure 1 gives the evolution of the atomic composition with the feed gas. When the ratio $R = NH_3/(NH_3 + N_2O)$ is lower than 0·4 the variation of the composition is weak. But from $R = 0{\cdot}4$ we observe a linear variation of Si, N and O. If the O/Si ratio is 2 for feed gas $R = 0$, the N/Si is not over 1 the N/Si ratio is lower than that of silicon nitride (Fig. 2) and then when $R = 1$.

2.3 Refractive index

The refractive index n of the layers with different composition has been measured with an ellipsometer Plasmos SD 2300. The wave length is $\lambda = 632{\cdot}8$ nm. Figure 3 gives the values of the refractive index for two thicknesses of the layer (about 100 and 600 nm). The first observation is that the refractive index has the same value whatever the thickness is. Second, n varies between 1·5 for the silicon oxide film to 1·80 for the silicon nitride one. Third, the variation of n is not linear. Blain *et al*[9] suggest that this behaviour is due to a variation of the density which is not a simple linear average between the density of SiO_2 and Si_{3N_4}. It is necessary to take into account the increase of the Hydrogen amount, displayed in FTIR, when the compound contains more and more nitrogen.

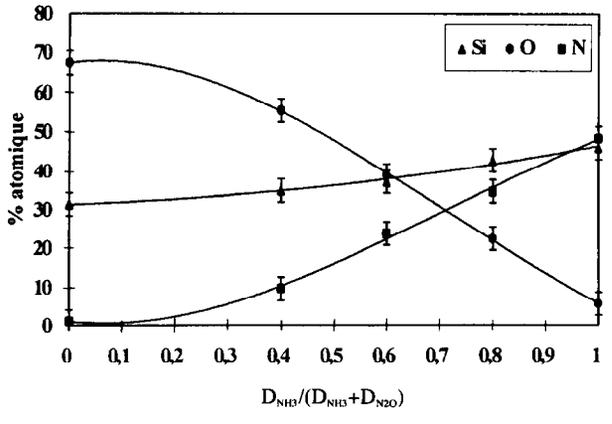

Fig. 1. Composition variations of PECVD SiO_xN_y layers.

2.4 Grazing X-rays reflectometry and density

The technique uses the reflection of X-rays at grazing angles.[10,11] The critical angle of total reflection is in relation with the density of the material deposited. We used a SIEMENS D5000 diffractometer with a reflectometry attachment. Three layers have been studied with this technique, their compositions correspond to:

- a silicon oxide film ($R = 0$ and thickness = 131 nm);
- a silicon nitride film ($R = 1$ and thickness = 114 nm);
- a silicon oxynitride film ($R = 0{\cdot}5$ and thickness = 93 nm).

Figure 4 gives the results of the reflection curves and their simulation with a SIMPLEX procedure. Table 1 compares the theoretical and the determinated values of density as well as the comparison of the thicknesses measured by ellipsometry and reflectometry. It is evident that the thicknesses determined by reflectometry are very close to that measured by ellipsometry. On the other hand the density values are very far from the theoretical values : the density of SiO_x:H is higher than that of SiO_2 and the density of SiN_y:H is lower than that of Si_3N_4.[12,13]

3 Discussion

XPS and FTIR analyses[8] are consistent with the Random Bonding Model described by Philipp.[14–17] In this model the deposited material would be constituted by a disordered network and a statistically arrangement of tetreadra $SiSi_xO_yN_z$ with $X + Y + Z = 4$.

The refractive index n and the $N/(N+O)$ ratio in the layer are not linked by a Bruggeman relation. For similar compounds, Knolle[18] considers that silicon oxynitrides thin films are made of a silicon phase and a phase with all the other elements. If we plot the n value as a function of the silicon percentage in the material, the n variation cannot be described by the Knolle's relations: the n index does not vary between 0·35 and 0·45% of silicon,

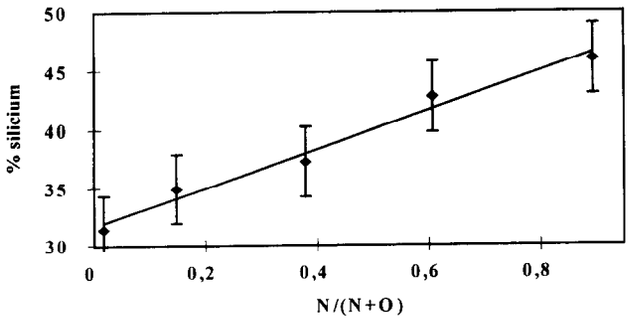

Fig. 2. Linear relation between N/(N + O) and Silicon amount in the layers.

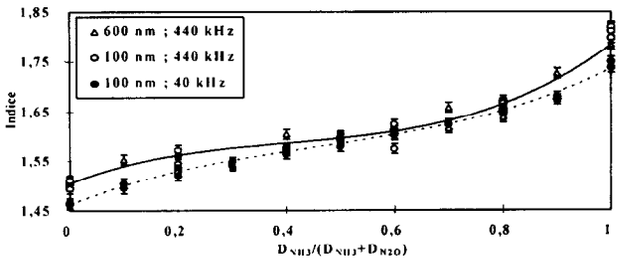

Fig. 3. Refractive index variations of silicon oxynitride layers (differents thicknesses and different excitation frequencies).

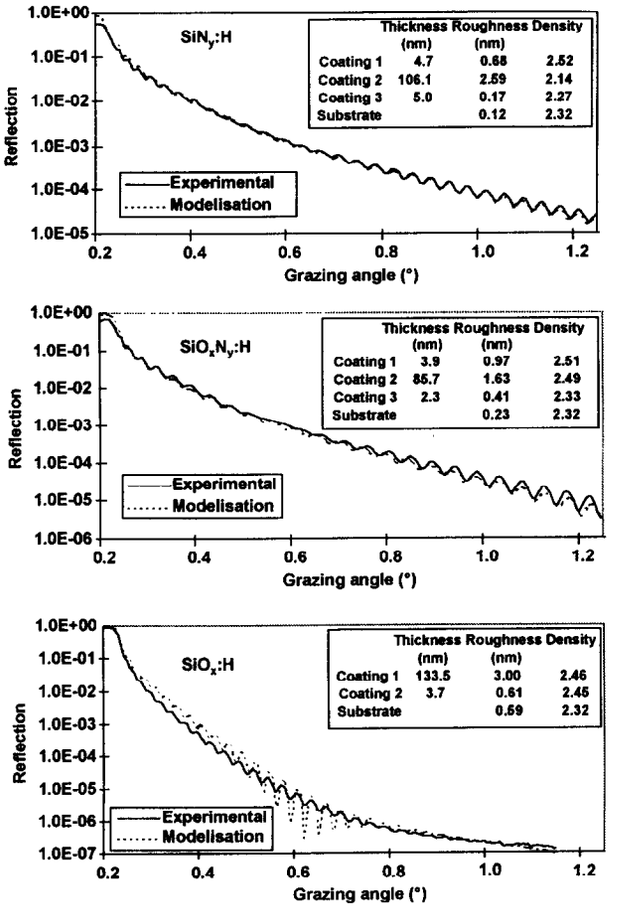

Fig. 4. Grazing X-rays reflectometry curves and modelisation of PECVD silicon nitride, silicon oxide and siliconoxynitride.

the composition of the silicon nitride corresponds to Si/N = 1 (higher than Si_3N_4), the n index and the density are lower than that of silicon nitride (Si_3N_4).

We want to determine the variation of the refractive index n as a function of the N/(N+O) ratio in the thin layer. Our starting point is the hypothesis that our material is a mixture of three phases: SiO_2-Si_3N_4-Si even if this is not true. We do not consider hydrogen enclosed in the layer and the compound will be written : $(Si)_u(SiO_2)v(Si_3N_4)$. From two layers of which the density, the refractive index and the composition N/(N+O) are known, it is possible to calculate the proportion of Si phase. The variations of Si proportion and density will be arbitrarily fixed. We want to separate the composition and the compacting effects so we will use the Bruggeman relation[18] for the n calculation as a function of the composition and the Clausius-Mossoti equation[19,20] for the density influence.

The principle is to calculate the index of a 'dense' layer with the same composition as the thin film. Starting from N/(N+O) the proportions of SiO_2, Si_3N_4 and Si are determined. The index of an SiO_x film ($(Si)_u(SiO2)_v$) with the same proportion of Si as the silicon oxynitride is calculated. The same calculation is made for an SiN_y film. With these two n values it is possible to calculate the index of a 'dense' oxynitride layer. The relation used is:

$$f_1 \frac{n_1^2 - n^2}{n_1^2 + 2n^2} + (1 - f_1) \frac{n_2^2 - n^2}{n_2^2 + 2n^2} = 0$$

with: f_1 the volumic fraction of phase 1; n_1 and n_2 the refractive indexes of phases 1 and 2.

The resolution of the Bruggeman equation leads to:

$$n_{Brugg} = \left\{ \frac{1}{2} [n_1^2(3f_1 - 1) + n_2^2(2 - 3f_1)] + \sqrt{[n_1^2(3f_1 - 1) + n_2^2(2 - 3f_1)]^2 + 8n_1^2 n_2^2} \right\}^{\frac{1}{2}}$$

The relation between the volumic fraction f_1 and the molar fraction x_1 is :

$$f_1 = \frac{v_1}{v_1 + v_2} = \frac{\frac{x_1 M_1}{d_1}}{\frac{x_1 M_1}{d_1} + \frac{(1-x_1)M_2}{d_2}}$$

with : M_1 and M_2 the molar weight and d_1 and d_2 the density.

We suppose that the variations of the density of the 'dense' layer are linear, and finally introduce

Table 2. Parameters used for refractive index calculation

	n_{Sio2}	d_{Sio2}	n_{Si3N4}	d_{Si3N4}	n_{si}	d_{si}
Dense material	1·46	2·2	2·02	2·8	3·6	2·31
	n_{SiOx}	d_{SiOx}	n_{SiNy}	d_{SiNy}		
PECVD layer	1·5	2·45	1·78	2·15		

Table 3. Calculated excess of silicon in SiN_y and SiO_x thin films (Bruggeman model)

	Composition		*Molar weight* ($g\ mol^{-1}$)	*Theoretical indexes and densities of the 'dense' layers with the same excess of Silicon*	
SiO_x	Si excess	O/(O+Si)	M_{SiOx}	n_{SiOx}	d_{SiOx}
	0·00	0·67	20·0	1·46	2·20
SiNy	Si excess	N/(N+Si)	M_{SiNy}	n_{SiNy}	d_{SiNy}
	0·08	0·52	20·67	2·19	2·76

the density measured by reflectometry of the film in the Clausius-Mossoti relation for the calculation of the refractive index.

Refractive indexes and densities of SiO_2, Si_3N_4 and Si are coming from the bibliography. Refractive indexes and densities of SiO_x and SiN_y PECVD films have been experimentally determined. These values are given in Table 2

The fitting of the calculated index and density with the experimental index and density leads to the layer composition and then the silicon excess of the SiO_x and SiN_y layers (Table 3).

The relation between the composition N/(N+O) and the refractive index of silicon oxynitrides takes into account:

(1) the density increases linearly from 2·45 to 2·49 then decreases linearly from 2·49 to 2·15;
(2) the silicon excess is 0 for $0 < N/(N+O) < 0{\cdot}6$ and exponentially increases between 0·6 and 1.

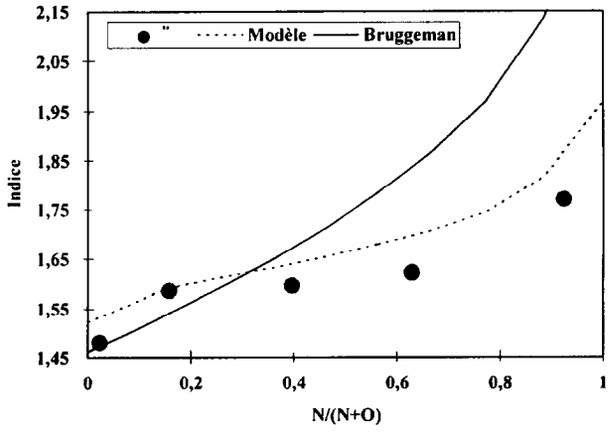

Fig. 5. refractive index modelisation of SiO_xN_y:H films.

The FTIR spectra show that an increase of the silicon content in the films is accompanied by an increase in the intensity of the Si-H absorption band. We consider that the Silicon excess follows the increase of the Si-H bond number.

The results given in the Fig. 5 show that the calculated refractive index is in good agreement with the experimental refractive index throughout the whole composition domain.

4 Conclusion

SiO_xN_y:H thin films were characterized by the variations of the composition, the refractive index and the density. These variations are not linear and it is necessary to take into account the increase of H levels when the composition goes from SiO_x:H to SiN_y:H. From the Bruggeman and Clausius-Mossoti relations, we could plot the evolution of the refractive index as a function of the layer composition N/(N+O).

References

1. Niklasson, G. A., Granqvist, C. G. and Hunderi, O., *Applied Optics* 1981, **20** (1), 26.
2. McLachlan, D. S., Blaszkiewicz, M. and Newnham, R. E., *Journal of the American Ceramics Society* 1990, **73** (8), 2187.
3. Bruggemann, D. A. G., *Ann. Phys.* 1935, **24**, 636.
4. Heavens, O. S., *Optical Properties of Thin Solid Films.*, Dover Publ., Inc. New York, 1965.
5. Born and Wolf, *Principles of optics.*, Pergamon, London, 1964.
6. Schoenholtz, J. E. and Hess, D. W., *Thin Solid Films* 1987, **148**, 285.
7. Blain, S., Klemberg-Sapieha, J. E., Wertheimer, M. R. and Gujrathi, S. C., *Canadian Journal of Physics*, 1989, **67**, 190.

8. Viard, J., Caractérisations de couches minces d'oxynitrures de silicium élaborés por PECVD, Thèse de Doctorat, Université Montpellier, 1996.
9. Blain, S., Klemberg-Sapieha, J. E., Wertheimer, M. R. and Gujrathi, S. C., *Canadian Journal of Physics* 1989, **67**, 190.
10. Kiessig, H., *Annalen d. Physik*, 1931, **10**, (7), 769.
11. Nevot, L. and Croce, P., *Rev. Phys. App.*, 1980, **15**, 761.
12. Mort, J. and Jansen, F., *Plasma deposited thin films*, CRC Press, Floride, 1986.
13. Ortega, L., Caractérisations por rayons X des isolants amorphes d'oxyritrues de silicium SiO_xN_yHz préparés en couches minces por PECVD, Thèse de doctorat, l'Université de Joseph Fourier, Grenoble 1, 1993.
14. Philipp, H. R., *Journal of Non-Crystalline Solids*, 1972, **8–10**, 627.
15. Philipp, H. R., *Solid State Communications 4*, 1966, 73.
16. Philipp, H. R., *Journal of Physics and Chemistry of Solids*, 1971, **32**, 1935.
17. Philipp, H. R., *Journal of the Electrochemical Society*, 1973, **120**(2), 295.
18. Knolle, W. R., *Thin Solid Films*, 1989, **168**, 123.
19. Ritter, E., *Applied Optics*, 1976, **15**(10), 2318.
20. Heitmann, W., *Applied Optics*, 1971, **10**(12), 2685.