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Determination of optical properties of a-SiO_xN_y thin films by ellipsometric and UV-visible spectroscopies

F Rebib¹, E Tomasella^{1,*}, J P Gaston², C Eypert², J Cellier¹, M Jacquet¹

1: Laboratoire des Matériaux Inorganiques, UMR CNRS 6002, Université Clermont-Ferrand 2, 24 Avenue des Landais, 63177 Aubière cedex, France.

2: Horiba Jobin-Yvon S.A., 5 avenue Arago, 91380 Chilly-Mazarin, France.

Eric.Tomasella@univ-bpclermont.fr

Abstract. Optical properties of silicon oxynitride thin films of variable composition were investigated. Their refractive index was found to decrease linearly from 1.94 to 1.46 when their composition varies between silicon nitride and silicon oxide. Spectroscopic ellipsometry showed that all samples were transparent over the visible range and that the layer structure also influences their optical properties. Using UV-visible spectroscopy, it was found that the film absorption decreases with increasing the oxygen amount in their composition. The optical gap determined from the transmission spectra showed high values increasing with the oxygen concentration. The Urbach energy was also estimated and linked to the film structure and composition.

1. Introduction

Silicon oxynitride thin films (SiO_xN_y) are a very promising material for both optical and electrical applications due to the possibility of tailoring their properties by acting on their elemental composition. Indeed, these materials are transparent in the visible range and their refractive index can be varied from one of silicon oxide (1.46) to that of silicon nitride (2.02) by only acting on the oxygen and nitrogen concentrations [1]. Their optical band gap could also be increased by increasing the oxygen amount [2].

A wide variety of deposition techniques and chemistries has been employed to steer the nitrogen and oxygen concentration in the silicon oxynitride composition [3, 4]. Reactive sputtering is a highly attractive method because it offers wide work possibilities [4, 5]. Recently, we reported a study of the sputtering process of a pure silicon target under argon-oxygen-nitrogen atmosphere and a reliable mean to obtain SiO_xN_y layers with a large stoichiometry variation [4]. The aim of this work is to show the potentialities of silicon oxynitride thin films deposited by reactive sputtering. For this reason, the SiO_xN_y refractive index and its dispersion were studied by single wavelength and spectroscopic ellipsometries. Their optical band gap and Urbach tails were determined using UV-visible spectroscopy.

* Corresponding author: Dr. Eric Tomasella, Laboratoire des Matériaux Inorganiques, UMR-CNRS 6002, Université Clermont-Ferrand 2, 24 Avenue des Landais, 63177 Aubière cedex, France.
Tel : +33473407337, Fax : +33473407108

2. Experimental procedure

A pure silicon target (99.999% purity, 100 mm diameter) was sputtered at 13.56 MHz frequency in an Alcatel SCM 450 sputtering equipment under different argon-oxygen-nitrogen gas mixtures. The total gas flow rate (F_t) was fixed at 5 sccm; argon flow rate was fixed at 70 % of F_t and the reactive gas flows were characterized using the ratio $R_F = F_{O_2} / (F_{O_2} + F_{N_2})$ (where F_{O_2} and F_{N_2} are the oxygen and nitrogen flows respectively). A sputtering power density (P) of 3.18 W cm^{-2} was used. Before each deposition, Si target was etched under pure argon atmosphere in order to remove any surface contamination. The layer composition was investigated by Rutherford Backscattering Spectroscopy (RBS) using 2 MeV alpha particles and a 15 nA current intensity. The refractive index was determined by mean of a Jobin-Yvon ELLISEL single wavelength ellipsometre ($\lambda = 632.8 \text{ nm}$). The results were completed with phase modulation spectroscopic ellipsometry measurements obtained with a Jobin-Yvon UVISEL FUV instrument in 190-826 nm (1.5-6.5 eV) spectral range. All ellipsometric measurements were done at a fixed incidence angle of 70° . To determine the optical band gap and Urbach energy, a double beam Perkin Elmer UV-visible spectrometer was used in the range of 200-1100 nm.

3. Results and discussion

RBS analysis showed that the silicon content remains almost constant; it only vary from 39 to 33 % when R_F increases from 0 to 0.5. So, the composition of SiO_xN_y deposits will be characterized considering only the ratio $x/(x+y) = O/(O+N)$, where O and N are the oxygen and nitrogen atomic concentration, respectively. As shown on figure 1, the composition of our films varies between those of silicon nitride and silicon oxide. Nevertheless, a small oxygen amount ($< 3 \%$) was detected even when no oxygen gas is introduced in the sputtering room. Residual gas and water vapour may be the source of these oxygen traces [4, 6].

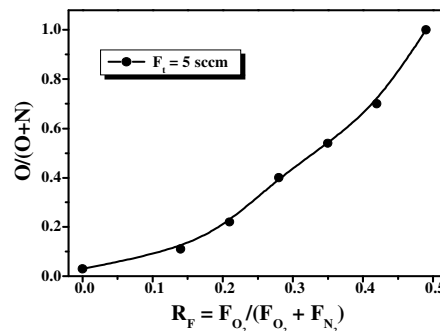


Figure 1. Variation of the atomic ratio of SiO_xN_y thin films as function of the reactive gases ratio.

Spectroscopic ellipsometry measurements allow calculating the complex index $\hat{n} = n + jk$ and the thickness d of a transparent layer. Measurements at a fixed wavelength give data to determine two of the three quantities n , k and d ; the third one should be known. However our deposits are transparent at 632.8 nm (so $k = 0$), so we could determine n and d at this wavelength with high accuracy.

The variation of SiO_xN_y films refractive index as function of their composition is shown in figure 2. This variation is quite linear following the equation: $n = 1.94 - 0.56 \times [O/(O+N)]$ (eq.1). The same behaviour was already reported for SiO_xN_y thin films obtained by PECVD [7]. Eq.1 is a little bit different from that obtained considering the massive material (Si_3N_4 and SiO_2) index values: $n = 2.02 - 0.56 \times [O/(O+N)]$; this difference is related to both structure and density of the layers [7].

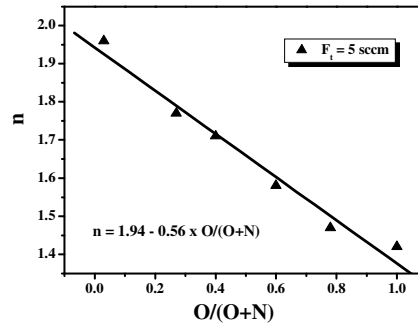


Figure 2. Variation of SiO_xN_y refractive index ($\lambda = 632.8$ nm) as function of their composition.

A Sharper approach was carried out by mean of spectroscopic ellipsometry measurements. To model the experimental data and access to the layer characteristics, the Tauc-Laurentz dispersion model [8] was used. It was found that the O-rich and N-rich layers showed more homogeneous structure than those with intermediate composition. Indeed, the ellipsometric data of these films were modeled considering a main SiO_xN_y layer covered with a very thin layer with lower index which corresponds to a post-deposition oxidation of the samples (figure 3a). Whereas, samples with intermediate composition exhibited an inhomogeneous interfacial region (figure 3b) probably resulting from the growing process. So, a three-layer model was used to fit their experimental characteristics. These results are in agreement with the structural analysis of the films [4].

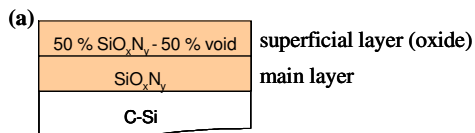


Figure 3a. Two layer model fitting the ellipsometric data of N-rich and O-rich SiO_xN_y thin films.

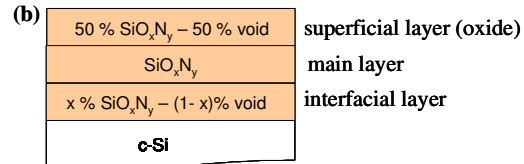


Figure 3b. Three layer model fitting the ellipsometric data of SiO_xN_y thin films with intermediate composition.

Definitively, the fitting of the ellipsometric data of the main SiO_xN_y gave the dispersion values of the refractive index and extinction coefficient values which are shown in figure 4. There is a good similarity between the experimental data and the adjusted curves. One could also notice that the extinction coefficient is negligible over the entire visible domain. These results confirm that the deposition conditions we set up at the beginning of this work allow to obtain silicon oxynitride thin films with high optical quality.

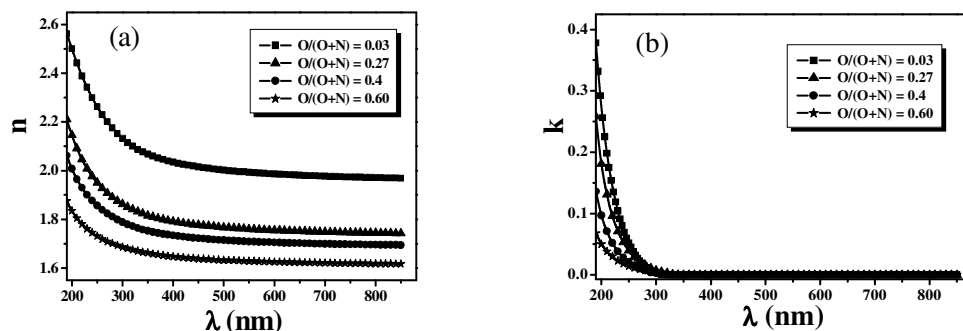


Figure 4. Dispersion of SiO_xN_y : (a) refractive index and (b) extinction coefficient.

The optical gap (E_g) and Urbach energy (E_u) were determined from the UV-visible transmission spectra (figure 5) using the Tauc relationship [9]. The O-rich films are more transparent and their UV absorption curves are truncated, so the determination of their E_g and E_u values is difficult. For the other samples, the results are summarized in table 1.

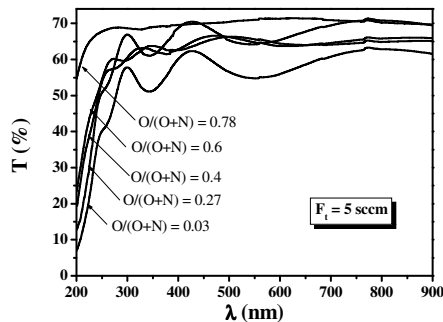


Figure 5. UV-visible transmission spectra of SiO_xN_y thin films.

O/(O+N)	E_g (eV)	E_u (eV)
0.03	5.86	0.6
0.27	6.22	0.63
0.4	6.33	0.9
0.6	> 6.4	
0.78		
1		

Table1. Optical gap (E_g) and Urbach energy (E_u) of SiO_xN_y thin films.

The optical gap values are higher than 5.8 eV and increases with O/(O+N) ratio. They are in agreement with those reported in literature; < 5 for silicon nitride and more between 7.5 and 9 for silicon oxide [10-12]. It was also reported that E_g is a very sensitive indicator of oxygen presence in the material [11]; this is in agreement with its increase with the oxygen concentration in our films. The Urbach energy seems to increase with increasing the oxygen content, but the trend could be validated since the values for O-rich films are missed and that the spectroscopic ellipsometry showed a more inhomogeneous structure for films with intermediate composition.

4. Conclusion

This study confirms the optical and dielectrical qualities of SiO_xN_y thin films deposited by reactive sputtering. Indeed, our samples were found to be transparent over all the visible range and their refractive index varies linearly with their elemental composition. This result stimulates the idea of layer with gradient in composition. Also, the large values of the optical band gap indicate that these materials could have good insulating qualities.

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