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XPS investigation of thin SiO_x and SiO_xN_y overlayers

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Abstract

Angle-resolved XPS is used to determine the thickness and the uniformity of the chemical composition with respect to oxygen and nitrogen of the very thin silicon oxide and oxynitride overlayers grown on silicon. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Angle-resolved XPS; Thickness determination; Siliconoxynitrides

1. Introduction

SiO_x and SiO_xN_y overlayers play a very important role in determining the performance of electrical and electro-optical devices and numerous workers have used different spectrocopic techniques for characterization and measurement of the thickness of these overlayers. For very thin overlayers (less than 15 nm) angle-resolved XPS is the preferred method [1–3] although Auger electron spectroscopy, ellipsometry, nuclear reaction analysis (NRA) and Rutherford backscattering (RB) are also employed [4–6]. Owing to the the presence of oxygen/water even under high vacuum conditions and the very high reactivity of silicon towards oxygen (during and/or after overlayer preparations) it is practically impossible to obtain overlayers devoid of oxygen [7]. In most cases this is not detrimental to materials performance and high-performance elctro-optical devices were fabricated.

In a previous study we reported the preparation, and photoluminesence and FTIR characterization of amorphous silicon (oxy)nitride overlayers on Si [8]. In this contribution we report the angle-dependent XPS measurements of the thickness of these very thin oxide and oxynitride overlayers.

2. Experimental

The samples were grown on (001) silicon substrates by plasma enhanced chemical vapour deposition (PECVD) at 100°C with nitrogen (N_2) balanced by 2% silane (SiH_4). The rf power and chamber pressure were 10 W and 1 Torr. Details of the preparation techniques as well as the photoluminesence properties are given in our earlier publication [8].

A Kratos ES 300 electron spectrometer equipped with a MgKα (not monochromatized) X-ray source at 1253.6 eV was used to record the spectra. The chamber pressure was kept below 5×10^{-9} Torr during analysis.

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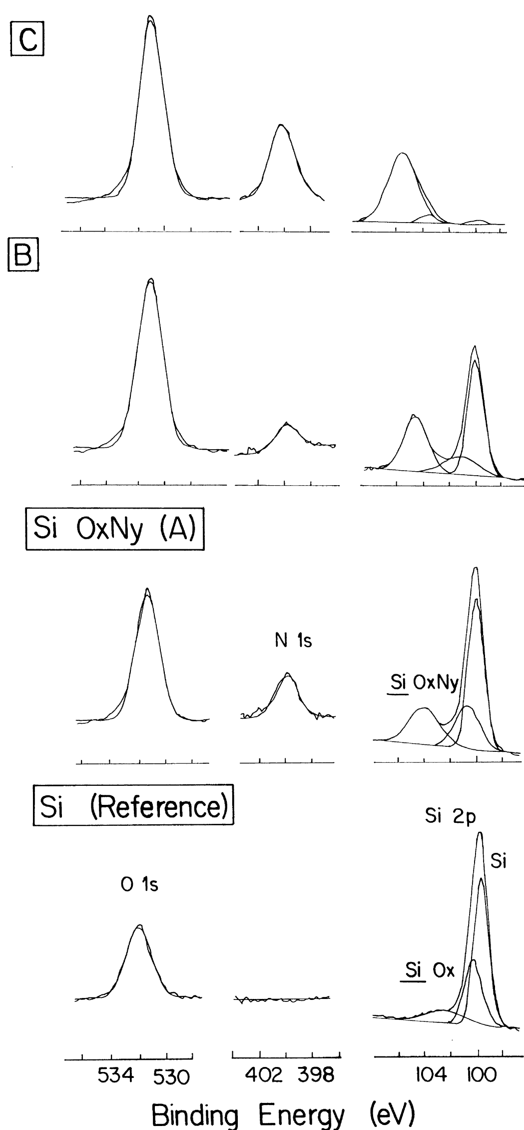

Fig. 1. O1s, N1s and Si2p regions of the XPS spectra of (001) Si substrate and 3 (A, B and C) siliconoxynitride samples.

3. Results and discussions

Part of the XPS spectra of three SiO_xN_y samples grown on Si with different thicknesses are shown in Fig. 1. The reference spectrum of Si is also included. As is evident from the spectra oxygen is present in all samples. The binding energy of N1s corresponds to N^- and O 1s to O^{2-} [7]. The Si 2p region consists of a metallic peak (Si^0) at low binding energy around 99 eV and another composite peak with varying binding energy of 103–105 eV which can be attributed to the oxide and/or oxynitride silicon (Si^{4+}) [7]. Owing to the limited resolution of our source/spectrometer further resolution between the oxidic and/or nitridic silicon was not possible.

Two spectroscopic questions, closely related to the fabrication and performance of the layers arise: (i) thickness of the overlayer, and (ii) uniformity of this overlayer with respect to its oxygen and nitrogen content. The thickness of the overlayer can be determined from the angular dependency of the two chemically different silicons, i.e. Si^{4+}/Si^0 as shown in Fig. 2. At low take-off angles intensity of the species in the overlayer (Si^{4+}) increase when compared with the species underlayer (Si^0). The dependence of the intensity ratio on the take-off angle is given by the expression:

$$I_{SiO_xN_y}/I_{Si} = K \times [1 - \exp(-d/\lambda_{SiO_xN_y} \sin \Theta)]/ [\exp(-d/\lambda_{SiO_xN_y} \sin \Theta)]$$

where K is the ratio $[n_{SiO_x}N_y\sigma_{SiO_x}N_y\ \lambda_{SiO_x}N_y/n_{Si}\sigma_{Si}\lambda_{Si}]$, n is the density of Si atoms in the corresponding layer, σ is the photoionization cross section, $\lambda_{SiO_x}N_y$ and λ_{Si} are the attenuation lengths of the photoelectrons in the overlayer and underlayer respectively, d is the thickness of the overlayer, and Θ is the take-off angle [1–3,6,9]. The validity of this approach was established; firstly by comparing the thickness of two SiO_2/Si samples obtained by this method against the thickness obtained by Rutherford Backscattering Spectrometry (RBS), and ellipsometry [6], and secondly by comparing the thickness obtained by XPS against the thickness obtained by Nuclear Reaction Analysis [2]. The molar volume of Si is 12.056 cm^3 and the molar volume of SiO_xN_y is approximated as 23.5 cm^3, from the molar volume of SiO_2, which has a wide range from 20 to 27 cm^3 depending on the crystal structure [10]. The reciprocal of the molar volume is taken as the density. Since the photoionization cross sections are inherently atomic the changes upon compound formation (in this case Si2p for Si^0 and Si^{4+}) are negligible such that they cancel out in the ratio [7,11]. Using the well established attenuation length values for both layers (λ_{Si} = 2.3 nm at 1151 eV, $\lambda_{SiO_x}N_y$ = 3.5 nm at 1146 eV) one obtains

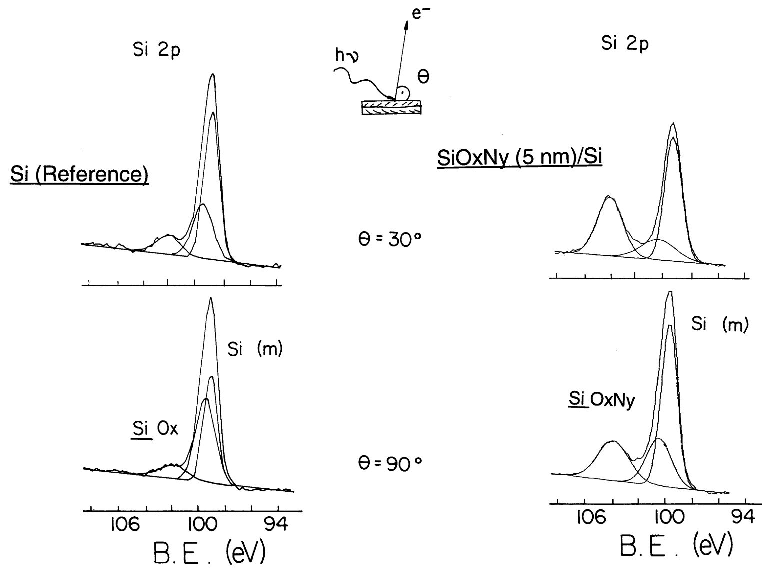

Fig. 2. Si2p region of the reference silicon and sample A recorded at two different take-off angles.

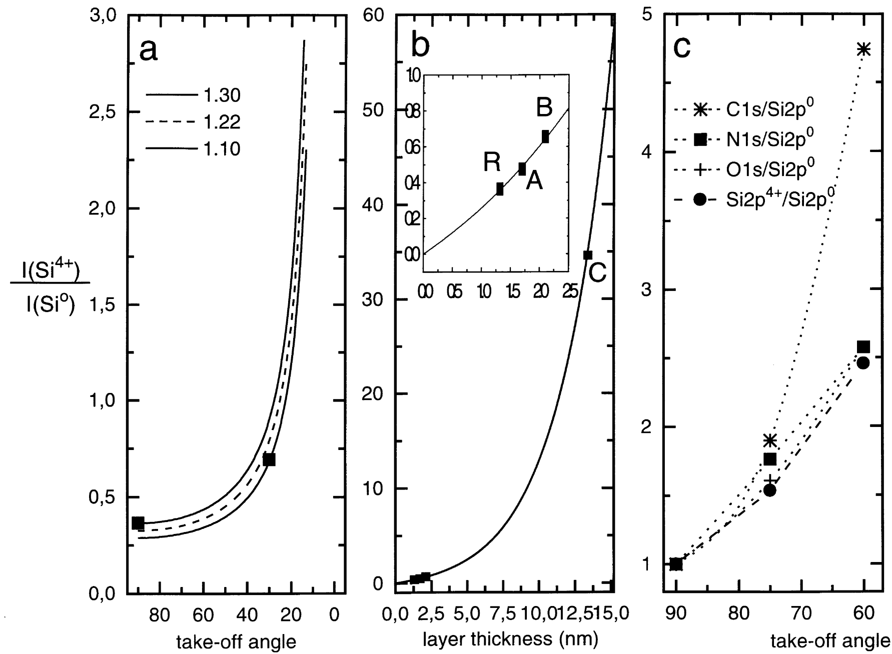

Fig. 3. (a) Theoretical curves for three different oxynitride overlayer thickness for the variation of the intensity ratio of Si^{4+}/Si^{0} together with measured ones (rectangles) as a function of the take-off angle. (b) Calculated Si^{4+}/Si^{0} ratio at 90° take-off angle and measured ones (R = silicon reference and oxynitride A, B and C samples). (c) Measured ratios (normalized to 90° values) of the $C1s/Si2p^{0}$, Si^{4+}/Si^{0}, $O1s/Si2p^{0}$ and $N1s/Si2p^{0}$ at different angles for the sample A.

the theoretical curves for thicknesses of 1.10, 1.22 and 1.30 respectively as depicted in Fig. 3(a). Our measured values (shown by rectangles) at two different take-off angles for the native oxide overlayer of the reference silicon sample matches the theoretical ones within an accuracy of 0.1 nm. Accordingly we can use the plot of Si^{4+}/Si^0 intensity ratios at 90° take-off angle for determining the overlayer thickness between 0–15 nm (Fig. 3(b)). Using this figure we can estimate the overlayer thickness of the samples shown in Fig. 1.

Sample	Measured Si^{4+}/Si^0 ratio	Estimated overlayer thickness (nm)
Si (reference)	0.37	1.2(1)
A	0.47	1.7(1)
B	0.65	2.1(2)
C	35	13(3)

The question as to the uniformity of the layers with respect to oxygen and/or nitrogen content can similarly be answered form the angle dependecy of the $O1s/Si2p^0$ and $N1s/Si2p^0$ signals as shown in Fig. 3(c) (all the ratios are normalized to the ratio at 90°). Introduction of the samples into the XPS chamber always incorporates hydrocarbon deposits which gives a C1s peak at 285.0 eV binding energy. Since hydrocarbon deposits are the outermost overlayer the ratio of the $C1s/Si2p^0$ displays the largest angular dependence as also shown in Fig. 3(c). The angular dependence of the Si^{4+}/Si^0 as well as $O1s/Si2p^0$ and $N1s/Si2p^0$ closely resemble each other and are completely different from the behaviour of the $C1s/Si2p^0$. This is a very clear spectroscopic indication that they all stem from the same overlayer, i.e. the oxygen and nitrogen content of the overlayer is uniform at least to XPS probing.

4. Conclusions

The well-established angle-resolved XPS measurements were used to determine the thickness of the overlayers in the range of 1–15 nm as well as to check the uniformity with respect to oxygen and nitrogen present in the overlayer since no other common spectroscopic methods are available in this range.

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