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XPS studies on SiO_x thin films

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The surface stoichiometry of SiO_x thin films ($x = 1$–2) has been studied by means of X-ray photoelectron spectroscopy. The presence of three Si oxidation states (SiO_2, SiO, Si_2O_3) has been observed through an analysis of the Si 2p line shape and the intensity variation of these different silicon oxide signals, as a function of the oxygen content, has been followed. The calculated stoichiometry has been compared with that obtained using the modified Auger parameter method. The good agreement between these results supports the validity of the modified Auger parameter as an easy and fast method to know the surface stoichiometry of SiO_x films.

1. Introduction

Silicon suboxide (SiO_x) thin films are widely used in several industrial applications, such as optical coatings [1], passivation layers [2] and insulating layers in Josephson junction integrated circuits [3]. For this reason a lot of work has been devoted to study the electronic and the structural properties of SiO_x [4], the growth of the SiO_x/Si interface [5] and the stoichiometry of SiO_x thin films as a function of the deposition parameters [6–8].

The possibility to know easily and quickly the surface stoichiometry of SiO_x is of fundamental importance for industrial applications. A well known technique to study the surface stoichiometry of thin films is quantitative X-ray photoemission spectroscopy (XPS) [9]. This method is not very simple to apply when overlayers of contaminants are present on the sample surface because (i) the normally used cleaning procedures to remove them, like noble-gas sputtering, can alter the real surface stoichiometry and (ii) the method introduced to take into account the presence of contaminants [10] can be used when the contaminant layer thickness is lower than the escape depth of the photoelectrons of the contaminant element.

In this work we report a method to establish easily the surface stoichiometry of SiO_x films, based on the modified Auger parameter calculated from XPS measurements [6]. We have compared the stoichiometric results obtained using this new procedure on evaporated silicon oxide samples (SiO_x, $x = 1$–2) with those calculated by using a careful fit procedure of the Si 2p peak which allows the determination of the intensities of the bound components involved in the SiO_x structure.

2. Experimental

Thin SiO_x films of different stoichiometry of about 600–700 Å thickness were prepared in high vacuum (10^{-5} Pa) by thermal evaporation of SiO grains onto clean glass surfaces kept at room temperature. Different stoichiometries were obtained by varying the evaporation rate from 5 to 20 Å s^{-1} (monitored using a quartz crystal microbalance). High oxygen contents were obtained introducing oxygen up to 10^{-1} Pa into the evapo-

ration chamber. The measurements were performed in a UHV apparatus at a pressure of $\sim 5 \times 10^{-8}$ Pa using an unmonochromatic Al X-ray source (1486.6 eV and 1 eV overall resolution) and a Perkin-Elmer spherical analyzer. The Auger and XPS spectra showed, within the limits of their sensitivity ($\lesssim 1\%$), the presence of carbon, silicon and oxygen only. In order to take into account the charging effects on the measured binding energies, we have referred all the spectra to the C 1s line ($E_B = 284.8$ eV).

3. Results and discussion

In XPS spectra, the modified Auger parameter α' of an element is defined as the sum of the kinetic energy (KE) E_K of the sharpest $Core_1$–$Core_2$–$Core_3$ ($C_1C_2C_3$) Auger transition and the binding energy (BE) E_B of the most intense core photoionization peak C_n ($n = 1$, 2 or 3), $\alpha' = E_K(C_1C_2C_3) + E_B(C_n)$ [11]. The reduced Auger parameter does not depend both on the reference level used in the spectra analysis, as Fermi and vacuum levels, and on the electrostatic charging effects of the sample, but it is very sensitive to the chemical environment of the excited element. We have chosen to use the Si 2p core level and Si $KL_{2,3}L_{2,3}$ Auger transition in order to calculate the α' parameter as a function of the oxygen content. This high-energy Auger transition has been excited by the bremsstrahlung radiation coming from the Al X-ray source.

In fig. 1 we report the Si 2p core level and Si $KL_{2,3}L_{2,3}$ Auger spectra for clean silicon and pure SiO_2 samples. The Si 2p core level shifts from 99.8 eV BE (clean silicon) to 103.8 eV BE (SiO_2) while the Si $KL_{2,3}L_{2,3}$ Auger transition moves from 1616.2 eV KE (Si) to 1607.7 eV KE (SiO_2). From these values we have calculated the reduced Auger parameters for Si ($\alpha' = 1716$ eV) and SiO_2 ($\alpha' = 1711.5$ eV) and we have introduced the parameter $\beta(x) = 1716 - \alpha'(SiO_x)$ which represents the variation of the reduced Auger parameter changing the concentration of the oxygen in the sample with respect to the pure silicon.

It has been shown that the Si 2p core level

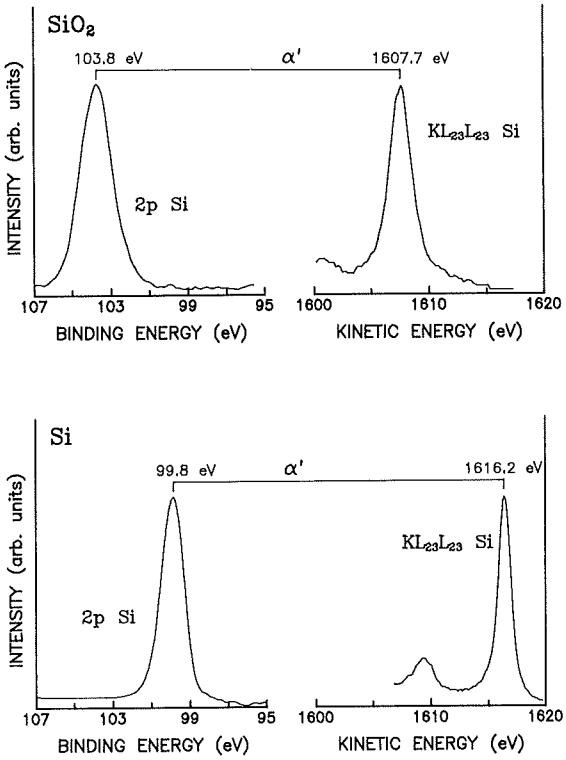

Fig. 1. Si 2p core level peak (left side) and Si $KL_{2,3}L_{2,3}$ Auger transition (right side) for pure SiO_2 (upper curves) and clean silicon (lower curves). α' parameters are also shown.

binding energy shifts almost linearly on going from Si to SiO_2 as a function of the oxygen concentration [5,7]. If we assume that the kinetic energy of the Si $KL_{2,3}L_{2,3}$ Auger transition shifts linearly when the oxygen amount increases from Si to SiO_2, also the parameter β varies linearly with the oxygen concentration, x, between 0 eV (Si) and 4.5 eV (SiO_2) following the relation:

$$\beta = 2.25x. \qquad (1)$$

Using the experimental values of the Si 2p core level binding energy and Si $KL_{2,3}L_{2,3}$ Auger transition kinetic energy of the different samples, we have calculated the parameter β for each sample and from eq. (1) the oxygen concentration x_β. These results are reported in the first two columns of table 1.

In fig. 2 we show the Si 2p core level (a), after background subtraction by means of a second-order polynomial curve, and the Si $KL_{2,3}L_{2,3}$

Table 1
Experimental β parameter, stoichiometry x_β determined using eq. (1) and stoichiometry x_{fit} determined using the fitting procedure

β	x_β	x_{fit}
2.10	0.93	0.99
2.35	1.05	1.15
2.80	1.24	1.26
3.05	1.35	1.37
3.35	1.49	1.51
4.00	1.78	1.69
4.30	1.91	–
4.68	2.08	1.97

Auger (b) spectra of the same samples reported in table 1, the clean silicon surface (lower curve), and the pure SiO_2 (quartz) sample (upper curve). In the 2p spectra, increasing the oxygen content, a continuous evolution towards higher binding energies of the main peak (attributed to Si–O bonds) and a decrease of the shoulder at lower binding energy (attributed to Si–Si bonds) are observed. The behaviour of the 2p spectra has already been reported [5,7,8] and the shift of the prominent peak towards higher binding energy, when the O/Si ratio increases, indicates an increase of the oxygen-richer components, such as Si_2O_3 and SiO_2. In the spectrum of the oxygen-richest sample ($x = 2.08$) the pure Si effect is almost completely suppressed, while the line shape and position of the main peak are in good agreement with those of a pure SiO_2 sample.

In order to check the utility of the modified Auger parameter to calculate the oxygen concentration in SiO_x samples, we have decomposed the Si 2p core level line into five different components by means of the least-squares fitting method. We have introduced five Gaussian functions, representing the four possible Si–O compounds (Si_2O, SiO, Si_2O_3 and SiO_2) and the pure Si peak, as described by the RBM model [12]. In fig. 3 we report the results of these fits for some of our experimental spectra. As the oxygen concentration increases, the Gaussian function representing the SiO_2 compound (curve D) becomes more and more intense. When the sample is near to the SiO_2, this component represents almost all the signal. The Si_2O component (not

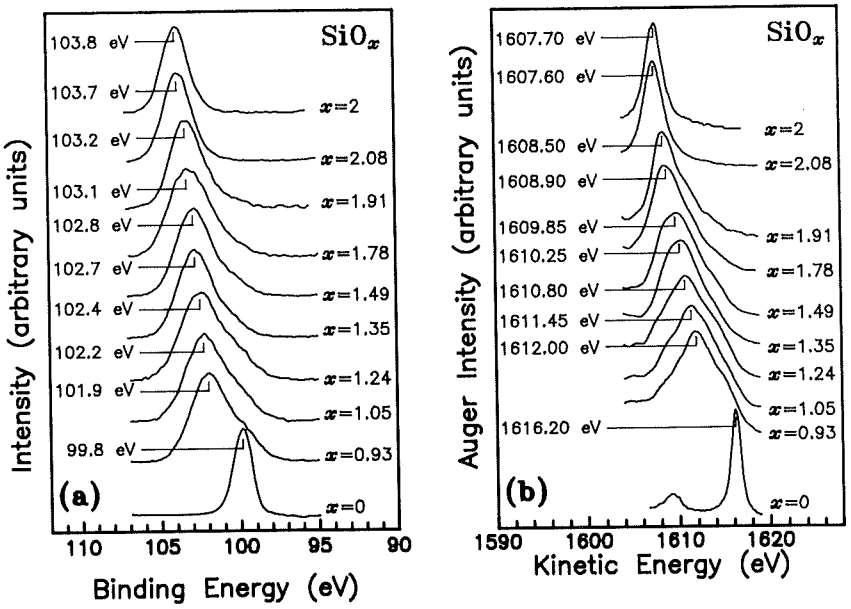

Fig. 2. (a) Si 2p core level peaks measured in SiO_x samples with different oxygen concentration x. (b) Si $KL_{2,3}L_{2,3}$ Auger peaks of the same sample reported in (a). On the left the binding energy (2p) or the kinetic energy ($KL_{2,3}L_{2,3}$) of the peak of each curve is reported, while on the right the x values, calculated using the β parameter in eq. (1), are shown. For comparison we have also shown the Si 2p and $KL_{2,3}L_{2,3}$ peaks for clean silicon (lower curves) and pure SiO_2 (upper curves).

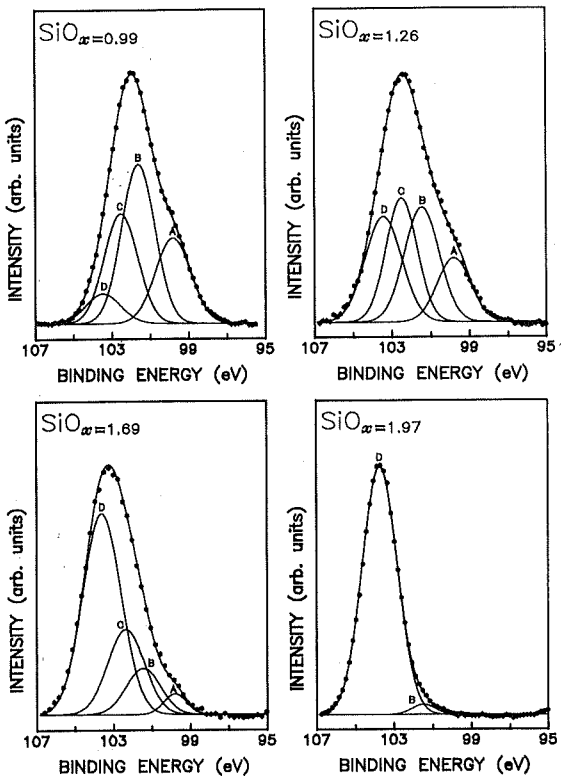

Fig. 3. Experimental Si2p peaks and their calculated Si–O components for SiO_x sample with different oxygen concentration x. The peak positions used in the fitting procedure are: Si: 99.8 eV, Si_2O: 100.7 eV, SiO: 101.5 eV, Si_2O_3: 102.5 eV and SiO_2: 103.5 eV. The shown x values have been obtained calculating the mean stoichiometry x_{fit} from the fitting results.

shown in the figure) is almost completely suppressed for all stoichiometries. This is in agreement with other results on thin SiO_x films [8], where this component was not observed, while it was always reported in SiO_x/Si interface studies [5], showing that the structure of evaporated SiO_x films is meaningfully different from that of a very thin oxidized-Si/Si interface.

From the results of this fitting procedure we have calculated the mean stoichiometry of our samples, x_{fit}, multiplying the relative intensity of the calculated Gaussian components with their own O/Si ratio (0 for Si, 1 for SiO, 1.5 for Si_2O_3 and 2 for SiO_2) and adding these terms. In this calculation we have supposed that the Si2p cross section is the same for all oxidation states of Si, which is true for the photon energy used in this work [5]. The estimated error on the x_{fit} values reported in the third column of table 1 is about $\pm 10\%$.

From table 1 one can observe the good agreement between x_{fit} and x_β, in all cases within $\pm 5\%$. These and previously published [6] results support our hypothesis of the linear dependence of the β parameter as a function of the oxygen concentration, suggesting the possibility of using this method to determine the surface stoichiometry of SiO_x films.

Our proposed method to calculate the surface SiO_x thin-film stoichiometry is easy to use, because it needs two XPS measurements only, and it does not require difficult data analysis; it is independent of the presence of unbound contaminants; the estimated error is lower than 5%, since this method is based on the measurement of the kinetic and binding energies of two well characteristic peaks on the XPS spectrum of the sample and it does not depend on the analyzer transmission function.

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