

Silicon wafer cleaning processes and ozone oxide growth as studied by angle-resolved x-ray photoelectron spectroscopy (ARXPS) and ellipsometry

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Knowledge of silicon oxide layer thickness and stoichiometry is essential for the integration of new dielectric materials. Among the various ways of obtaining ultrathin silicon oxides, chemically grown oxides are a promising choice. Different cleaning processes of silicon wafer for microelectronic integrated-circuit-scale application were investigated by XPS and ellipsometry. In this work, overlayer thicknesses were deduced from XPS intensity photoelectron lines and ellipsometric measurements. A comparison between these techniques was carried out. Chemical compositions of the overlayers were deduced from XPS measurements, and an ellipsometric calibration is proposed according to the relative oxygen atomic concentration. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: silicon; ARXPS; ellipsometry; oxide growth; ozone treatment

INTRODUCTION

Following the International Technology Roadmap for Semiconductors (ITRS), integrated-circuit (IC)-scale devices are decreasing drastically. It is now becoming a critical point to characterize properly the thickness of ultrathin silicon dioxide films that are integrated in a dielectric stack.

Thickness measurement and stoichiometry determination of the oxide films, as well as surface wafer chemical state after cleaning, are technologically important tasks. Optical ellipsometry usually is used in microelectronic fabrication for oxide overlayer thickness estimation because this method presents depth resolution down to the nanometre scale. Visible light ellipsometry shows high reproducibility but relies, especially for very thin layers, on the knowledge of a model structure for the interpretation.

The evaluation of oxide thickness requires a valid model that is influenced by the nature of the oxide and also by the interface chemical homogeneity, which is why we chose to compare ellipsometric results with those of XPS. X-ray photoelectron spectroscopy has long been used in the study of layer composition as a routine technique but it relies on a number of physical parameters such as the electron escape depth in order to allow the thickness of a layer to be determined.

Angle-resolved XPS (ARXPS) allows non-destructive depth profiling of very thin layers; this method is used

to identify the chemical nature of the oxide film, to detect a composition gradient through the film down to the interface and to estimate layer thickness.

A combination of XPS and ellipsometry seems to be necessary to gain some confidence in the thickness measurements on nanometre-scale oxide overlayers.

EXPERIMENTAL

Every wafer used in the experiment was prepared so as to be free of hydrocarbon (CH_x) and native oxide. A CARO (or sulphuric piranha mixture) process then was followed by HF treatment.

The definitions and properties of each wet chemical cleaning process^{1,2} are listed in Table 1.

The different cleaning processes characterized are described in Table 2.

Treated wafers were measured systematically in a clean room using an FE3 RUDOLPH monochromatic (633 nm) ellipsometer on 19 points and thickness was estimated with SiO_2 refractive index $n = 1.46$. Measurement uncertainty for this type of ellipsometer and for 1 nm thick layers is 0.1 nm.

Samples were analysed by ARXPS on an S-Probe system (Surface Science Instruments, USA) using the monochromatized Al $K\alpha$ photoelectron line.

RESULTS AND DISCUSSION

Both O_{1s} and Si_{2p} photoelectron lines were registered and the Si 2p lines were decomposed into different oxide components: SiO_2 and SiO_x , with $x < 2$ (Figs 1 and 2). From the Si 2p photoelectron line intensities corresponding to the

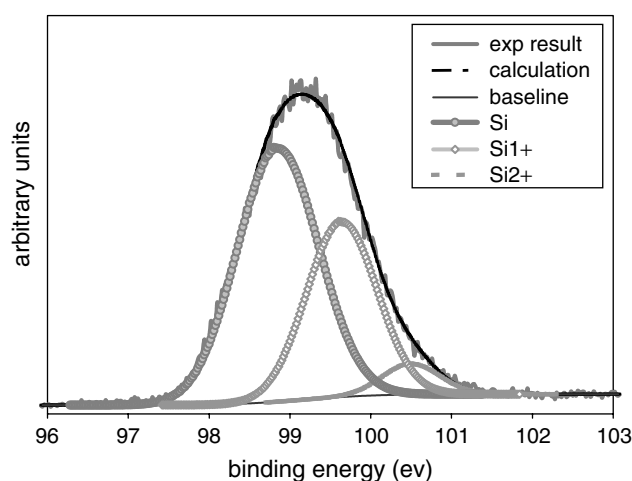
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Table 1. Major wet cleaning processes for advanced technology

Name	Process condition	Removal
CARO	[H ₂ SO ₄ , H ₂ O ₂]	Organic contamination
SC1	[NH ₄ OH, H ₂ O ₂ , H ₂ O]	Particles
SC2	[HCl, H ₂ O ₂ , H ₂ O]	Metallic contamination
RCA	SC1 + SC2	Particle and metal
HF last	HF 1%	Native oxide

Table 2. Experimental conditions

Cleaning processes	Temperature	Concentration	Time
CARO	110 °C, 180 °C	[3, 1]	10 min
RCA	70 °C	[0.25, 1, 5] + [1, 1, 5]	10 + 10 min
HF	20 °C	1%	1 min
O ₃		1 ppm	15 s, 40 s, 200 s, 10 min
O ₃		0.2, 6 and 16 ppm	10 min

**Figure 1.** The Si 2p photoelectron line of an 'HF last'-cleaned Si wafer.

Si wafer, suboxide and dioxide components, the thickness of the different layers t_i was deduced from Ref. 3 using

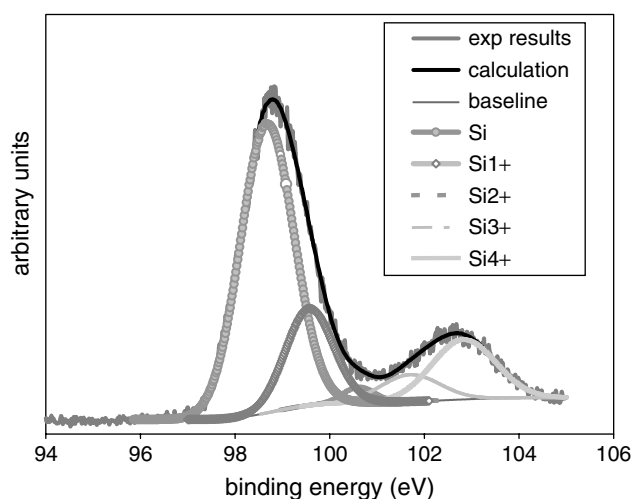
$$t_i = \lambda_{Si} \sin \theta \ln \left[1 + \left(\frac{I_{Si}^\infty}{I_{SiO_2}^\infty} \right) \left(\frac{I_{SiO_2}}{I_{Si}} \right) \right]$$

where λ_{Si} is the Si_{2p} photoelectron attenuation length, θ is the take-off angle, $(I_{Si}^\infty/I_{SiO_2}^\infty)$ is the intensity ratio from bulk silicon and silica samples ($=1.0 \pm 0.2$ on ten successive measurements) and (I_{SiO_2}/I_{Si}) is the intensity ratio of the Si_{2p} photoelectron lines from the cleaned samples.

For samples without a dioxide overlayer, the suboxide estimated thickness was deduced from the Si_{2p}[∞] attenuated signal I_{Si}

$$t_i = \lambda_i \sin \theta \ln(I_{Si}^\infty/I_{Si})$$

Background subtraction for integrated XPS peak intensities was conducted according to Shirley's procedure.⁴ In a first

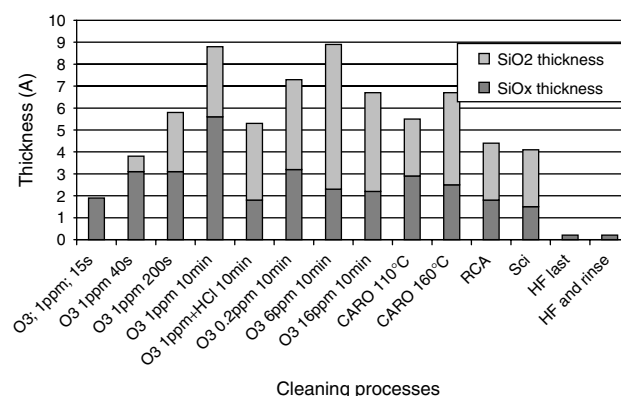
**Figure 2.** The Si 2p photoelectron line of an ozone-cleaned wafer (1 ppm, 200 s).

estimation the Si_{2p} photoelectron attenuation length was supposed to be the same for the Si wafer and for the oxide layer ($\lambda_{Si} = 2.6$ nm). No particular attention was paid to the most difficult problem of the difference between effective attenuation length (EAL) and electron inelastic mean free path (IMFP), nor for the absolute value of the EAL.⁵

Results are given for a take-off angle of 35 °C corresponding to an analysed thickness of 4.5 nm. These results are approximate, not only because of measurement uncertainties and curve proceedings but also because the thickness determination method supposes that the coverage layers are homogeneous and thicker than the photoelectron escape depth. However, according to the results obtained so far, the surface structure of the samples can be illustrated as shown on Fig. 3.

From the XPS results, it is possible to presume that in a first approximation nearly all the cleaning processes produce the formation of a 0.25 nm thick suboxide layer in a first step and then the oxide process goes on with SiO₂ growth.

Thickness measurement between ellipsometry and XPS is compared in Fig. 4, where quite good agreement is observed. The estimated uncertainties in XPS measurements are 20%, according to Ref. 6.

**Figure 3.** X-ray photoelectron spectroscopy oxide layer composition.

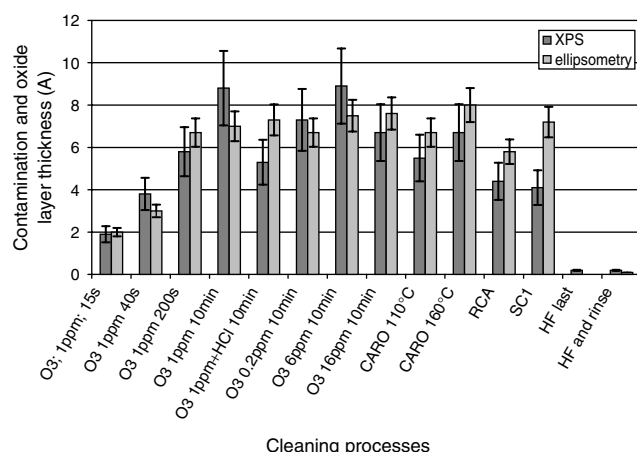


Figure 4. Ellipsometric and XPS thickness measurement comparison.

To be more precise, for the very small residual contamination in the case of sample 'HF last' or 'HF + rinse', the transfer function of the analyser was measured with a clean Si sample for five analysis angles from 15° to 90°. This value also was taken as the O_{1s} transmission function, in spite of the kinetic energy difference between Si_{2p} and O_{1s} photoelectrons. No surface-state structure effect was expected: the surface of the samples is amorphous and the signal is angular-integrated due to the large acceptance angle and the x-ray beam size ($1000 \times 250 \mu m^2$). An isotropic XPS photoelectron emission then is supposed. From these measurements the normalized area of the Si_{2p} photoelectron line $NA(Si)$ was deduced and the transmission function $F(\theta)$ determined (Fig. 5)

$$F(\theta) = NA(Si_{2p})(\theta) / (VN_{Si}SF_{Si}\lambda_{Si})$$

where V is the analysed volume, N_{Si} is the number of Si atoms contained in a primitive cell and SF_{Si} is the sensitivity factor of Si_{2p} .

Both SF_{Si} and SF_O were determined experimentally from a reference SiO_2 sample and are found to be 0.8 and 2.99, respectively. The transmission function $F(\theta)$ was found to be 1.8×10^{-11} for $\theta = 35^\circ$.

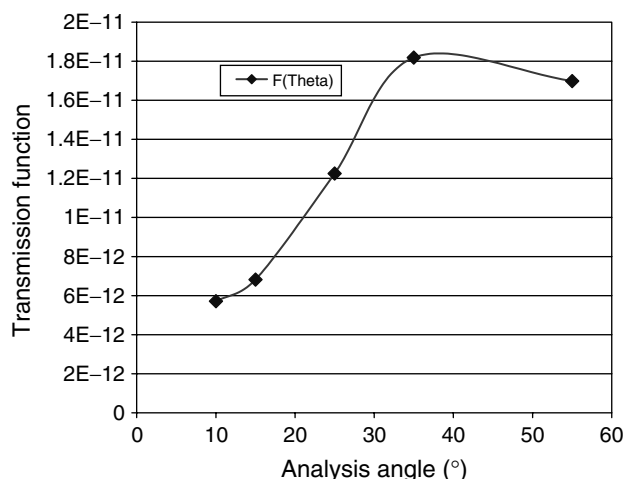


Figure 5. Analyser transmission function $F(\theta)$.

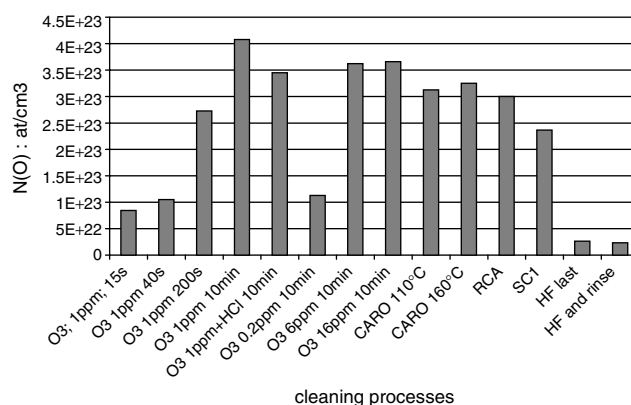


Figure 6. Oxygen atom density versus cleaning processes as measured by XPS.

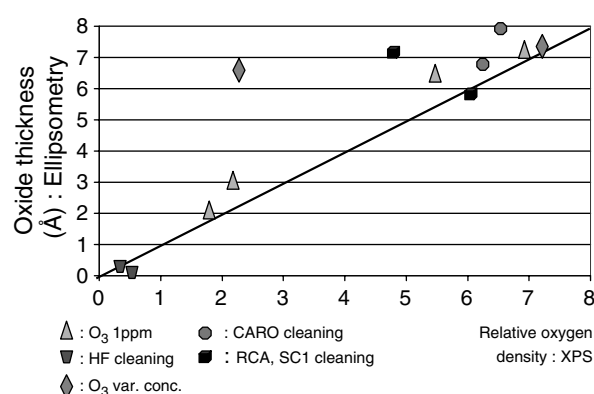


Figure 7. Relationship between oxide layer thickness as measured by ellipsometry and relative oxygen density as measured by XPS.

Absolute values $N(O)$ of the oxygen atoms then were determined from the O_{1s} spectrum normalized area $NA(O)$

$$N(O) \text{ atoms cm}^{-2} = NA(O) / [VSF_O F(\theta)]$$

with a mean free path for O_{1s} of 1.96 nm (Fig. 6).

It is then possible to make a correspondence between the thickness measurement by ellipsometry and the XPS oxygen concentration obtained by dividing $N(O)$ atoms cm^{-2} by the number of Si atoms present in a $Si(100)$ primitive cell (5×10^{22} atoms cm^{-2}).

In Fig. 7, the measured thickness obtained by ellipsometry is presented as a function of the relative oxygen density determined by calculation from the XPS results.

Most of the measurements realized on various cleaning processes (except for O_3 at various concentrations) show a linear relationship between experimental results and calculation. Accordingly, it is possible to propose a calibration of ellipsometric measurements with an approximate estimation of oxygen density.

CONCLUSION

An overview of various cleaning processes and wet chemical oxide production can be deduced from XPS and ellipsometric measurements. For all the studied oxides, measured thicknesses were found to be <1 nm with an interfacial suboxide

layer. As expected, the thinnest oxide layers were measured on wafers treated with 'HF last' or 'HF + rinse'. For ozone-prepared oxides, limitation of the interfacial layer thickness is reached by increasing the ozone concentration.

A combination of two surface-sensitive analytical techniques gives the opportunity to measure nanometre-scale Si wafer overlayer thickness and to obtain information about the chemical structure of these layers in term of suboxides.

In spite of the fact that we are unable to give a true uncertainty budget of XPS measurements (and spectrum processing) and ellipsometric measurements, good agreement between these two measurements is obtained for the estimation of thin-film thickness. In this paper we show that XPS can be used to calibrate ellipsometry measurements according to the oxygen density contained in the top layers

of the films, and an estimation in term of oxygen-covering monolayers can be proposed.

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