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ARXPS analysis of silicon oxide films

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Angle-resolved X-ray Photoelectron Spectroscopy (ARXPS) has been performed on (100) Si surfaces in different conditions as regards the oxides nature - native oxides, thermally formed oxides, and also after a cleaning procedure by Ar^+ ion sputtering (e.g. E= 2 keV). The most sensitive angle to surface oxidation states (Si^{1+}, Si^{2+}, Si^{3+}, Si^{4+}) was the take-off-angle (TOA): 25^o. Native oxides and thermally oxide phases on Si surfaces consists in a mixture of Si_2O, SiO, Si_2O_3 and SiO_2. The XPS measurements have putted into evidence a higher concentration of suboxides in high oxidation state (Si^{3+}) on naturally oxidized Si substrates. The thermally oxidized Silicon surfaces contain suboxides in a low oxidation state (Si^{1+}). The Ar^+ ion sputtering removed rapidly the superficial silicon oxides. The analysis and computation of SiO_2 film thickness on crystalline Silicon was done in the frame of modified Bethe equation for Electron inelastic mean free path (IMFP) and taking into account the intensity of SiO_2 peak and Si peak together with the TOA in the XPS measurement. Native oxide thickness for SiO_2 was d_{oxy} ~ 24Å and for thermally oxidized sample was d_{oxy}~ 27Å. Due to the slightly difference in the nature oxidation states it is suggested that the silicon dioxide appeared from two different kinetics in the oxidation processes.

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1. Introduction

X-ray photoelectron spectroscopy (XPS) offers several key features which makes it ideal for characterizing ultra-thin oxide films. The relatively low kinetic energy of photoelectrons (< 1.5 keV) makes XPS inherently surface sensitive in the range (1-10 nm). Secondly, the energy of the photoelectron is not only characteristic of the oxidation state of the atom (as an example the electrons emitted from $2p_{3/2}$ shell in SiO_2 are present approximately 4 eV higher in binding energy than electrons from the same shell originating from Si^0 (bulk Si). In the third place the XPS has the advantage that it is straightforward to quantify through the use of relative sensitivity factors that are largely independent of the matrix.

Due to its dominant role in silicon devices technologies [1], the SiO_2/Si interface has been intensively studied in the last five decades. Native oxidation of Si is known to have detrimental effects on ultra-large-scale-integrated circuit (ULSIC) processes and properties, including metal/Si ohmic contact, the low-temperature epitaxy of silicide, and dielectric breakdown of thin SiO_2 [2]. According to many previous studies [1] the structure of this interface contains two distinct regions. The near interface consists of a few atomic layers containing Si atoms in intermediate oxidation states i.e. Si^{1+} (Si_2O), Si^{2+} (SiO) and Si^{3+} (Si_2O_3). A second region extends about 30Å into SiO_2 overlayer. The SiO_2 in this layer is compressed because the density of Si atoms is higher for Si than for SiO_2 [1]. The HF treatment is efficient in suppressing the growth of native oxide on Si due to the presence of a Si-H bond formed at the end of a dangling bond. As a consequence the surface reactivity is low and it is possible to prevent the formation of silicon-oxygen bond [2]. The SiO_2 film thickness can be determined by XPS technique**.** Oxide thickness in the initial stage of native oxidation is too thin for a quantitative analysis. This it happens because Si^{x+} peaks ((photoelectrons from SiO_x (0<x<2) which is the key material in initial oxidation) are indistinct and buried in a small peak of Si^4 (photoelectrons from SiO_2) and a foot of Si^0 (photoelectrons from bulk Si).

There are a number of analytical techniques capable of measuring oxide thickness on films < 10 nm thick as included :XPS, AES, SIMS, RBS,TEM, Nuclear Reaction Analysis(NRA), Spectroscopic Ellipsometry (SE) and capacitance-voltage (CV) measurements. The effective attenuation length (EAL) is the key-material-dependent parameter needed for measurements of film thickness by XPS [3]. The EAL differs from the corresponding inelastic mean free path (IMFP) on account of elastic scattering of the signal electrons. In addition, the EAL depends on film thickness, electron emission angle and XPS configuration [4, 5].

The ARXPS measurements offer the possibility to study compositional changes at different depth amplitude from the surface for the analyzed sample.

The aim of this paper is to explore the possibilities of angle-resolved XPS (ARXPS) technique in performing quantitative analysis of SiO_2 layers thermally grown and also naturally oxidized on silicon single-crystalline surfaces.

2. Experimental

A first set of silicon samples (100) Si was exposed to a naturally oxidation process for a long time decade (years) in atmosphere. A thin layer of native oxide was grown that was firstly putted into evidence by a color surface change.

A second set of Si (100) samples were exposed to an air flow in an open furnace at $T=700^0C$ for $t_1=2$ h and $t_2=5$ h. The thermally oxidized films (mostly SiO_2) were blue like color.

The SiO_2/Si interface was studied by ARXPS technique. In this view the photoelectron spectra were recorded using a VG EECSA 3MK II machine with X-rays emitted by an anti-cathode of Al ($E_{k\alpha}=1486.7$ eV). A hemispherical analyzer was operated in the constant-energy mode with a pass energy of 10 eV giving an energy resolution of 1.18 eV, which was determined as the FWHM (full width half maximum) of the Au 4f7 peak. The analysis chamber was maintained at ultra high vacuum (~ 10^{-9} torr) and for ARXPS analysis the electron take-off angle (TOA) was defined in accord to ASTM document E-673-03 related to Standard Terminology Relating to Surface Analysis, as the angle at which particles leave a specimen relative to the plane of the specimen surface. In our experimental set-up we measured the angle between the analyzer axis and the specimen surface an angle which is congruent with TOA as angles with perpendicular sides. The TOA angles were varied in the steps: 25^0, 55^0 and 75^0.

The XPS recorded spectra were processed using Spectral Data Processor v 2.3 (SDP) software. In its structure SDP soft uses for the deconvolution of XPS line a specific ratio between Lorentzian and Gaussian shape and these characteristics ensures a good fit of experimental data. As the standard practice in XPS studies the C_{1s} line (285 eV) corresponding to the C-C bond has been used as reference Binding Energy (BE) [6].

In Fig.1 is presented the TOA angle considered in the equation for oxide thickness evaluation as presented in [2, 7, 8, and 9].

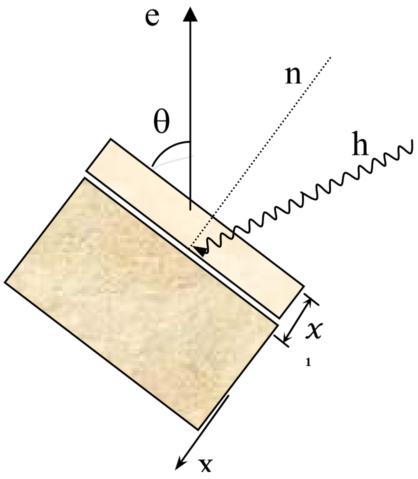

Fig.1. Sample characteristics in ARXPS measurement.

The oxide film thickness d_{oxy} is determined by the Si 2p core level intensity ratio of the oxidized silicon film I_{oxy} and substrate silicon I_{si} by:

$$d_{oxy}=\lambda_{oxy}\sin\theta[I_{oxy}/(\alpha I_{Si})+1] \qquad (1)$$

reference [10]
where

$$\alpha=I_{oxide\infty}/I_{si\infty}=0.76 \qquad (2)$$

The value for this ratio was experimentally obtained taking into account the intensity for the line SiO_2 (Si^{4+}) in a thick layer of oxide (where the signal for the bulk silicon is not present) reported to the intensity of Si^0 line in bulk silicon (where the oxide do not exists e.g. after Ar^+ ion sputtering).

It is well known however that large discrepancies exist for the photoelectron effective attenuation length in SiO_2 where values from 2 to 4 nm have been reported and compared to theoretical prediction for the inelastic mean free path. The ARXPS measurements are dependent on the value of sinθ, and the ratio I_{oxy}/I_{Si} will be computed only for SiO_2 oxide (Si^{4+}). The electron inelastic mean free path (IMFP) λ is analyzed and computed in terms of the Bethe equation for inelastic scattering which can be written [11]:

$$\lambda=E/\,[E_p^2\beta\ln(\gamma E)]\ \text{Å} \qquad (3)$$

For electrons in the range (50-200) eV [7, 8] the computed IMFP is presented in the form of TPP-2M formula:

$$\lambda=E/\,\{E_p^2\,[\beta\ln(\gamma E)-C/E+D/E^2]\} \qquad (4)$$

E-electron energy (in eV)

$$\begin{aligned}&\beta=-0.10+0.944/(E_p^2+E_g^2)+0.069\,\rho^{0.1}\\&\gamma=0.191\,\rho^{-0.50}\\&C=1.97-0.91\,U\\&D=53.4-20.8\,U\end{aligned} \qquad (5)$$

$U = N_V\rho/A$ (N_V- total number of valence electrons per atom or molecule, ρ- density (gcm^{-3}), A- atomic or molecular weight, E_g-band gap, E_p- plasmon energy).

For E_p which is the free- electron plasmon energy (in eV) it was used the formula

$$E_p=28.8\,(\rho N_V/A)^{1/2}\ \text{eV} \qquad (6)$$

as is mentioned in reference [9].

For compounds N_V is calculated from the sum of contributions from each constituent element (i.e. N_V for each element multiplied by the chemical or estimated stoichiometric coefficient for that element) [7].

The native oxidized silicon samples (namely SO 00) and thermally oxidized silicon samples (SO 10 and SO 20) were exposed to an Ar^+ ion sputtering process at different voltages and different etching times. It is observed the evolution of different suboxides species and the variation of oxide film thickness.

3. Results and discussion

In Figure 2 the Si 2p spectra present two lines where the lower binding energy is associated with Si^0 (bulk) and the higher binding energy is associated with silicon dioxide. The Si 2p oxide line intensity increases with the increase in oxide thickness, while the Si 2p substrate line intensity decreases.

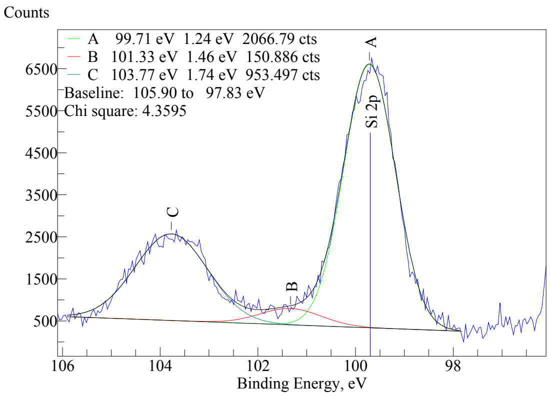

Fig. 2. Si 2p spectra for Si $^{4+}$(SiO_2-A) and Si^0(bulk-C).

In Fig. 3 are presented the Si 2p lines in crystalline silicon and in silicon oxides for the spectra taken at TOA: 25^0, 55^0 and 75^0 for native oxides. As a general remark in superimposed spectra as the TOA increases the signal from Si^0 (bulk) is more prominent.

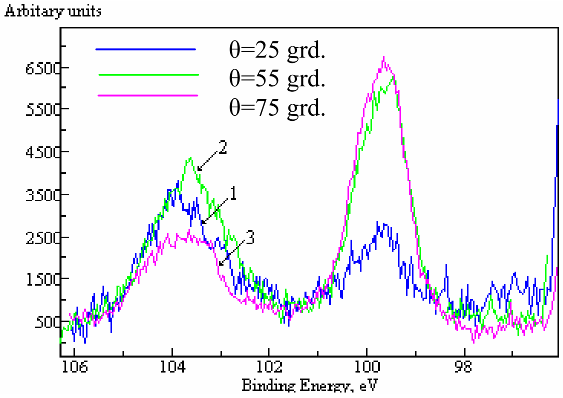

Fig.3 SiO_2/Si native oxides XPS proportional spectra

For the sample SO 00 the deconvolution for Si core levels 2p lines are related with specific Binding energies (BE) for Si^0 (A), Si^{1+} (Si_2O- B), Si^{2+} (SiO-C), Si^{3+}(Si_2O_3- D) and Si^{4+} (SiO_2- E), as presented in Figure 4 at TOA=25^0.

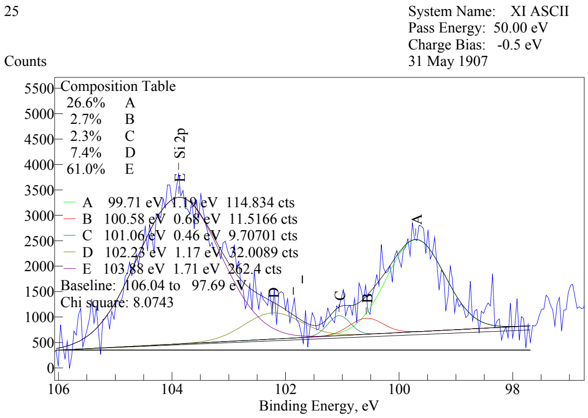

Fig. 4 XPS spectra for SO 00 sample at TOA=25^0.

In Table 1 is presented the comparative contribution for silicon dioxide and silicon suboxides for SO 00 (silicon sample with native oxides) and for SO 20 (silicon sample that was oxidized at 700^0C for 2 hours in air)

Table 1.

Oxidation states for Si	Results in our experiment BE (eV) SO 00 SO 20		Reference [1]	Composition table (%) SO 00 SO 20	
Si^0	99.7	99.71	99.5	26.6	19.9
Si^{1+}	100.58	100.57	100.45	2.7	7.6
Si^{2+}	101.06	101.58	101.25	2.3	2.5
Si^{3+}	102.23	102.38	101.98	7.4	3.4
Si^{4+}	103.88	103.94	103.40	61	66.5

As it was mentioned [1], the structure of the interface SiO_2/Si consists in two regions. The near interface contains few atomic layers of Si atoms in intermediate oxidation states i.e. Si^{1+}(Si_2O), Si^{2+}(SiO) and Si^{3+}(Si_2O_3). A second region extends about 30 Å into SiO_2 overlayer [1]. The SiO_2 in this layer is compressed because the density of Si atoms is higher for Si than for SiO_2. As a general remark, we assert that although the deconvolution has a slight arbitrary degree, in the SO 00 sample it prevails the suboxides with high oxidation states (e.g. Si^{3+}) and in SO 20 sample it prevails the suboxides with lower oxidation states (e.g. Si^{1+}). This fact is a possible result of different oxidation kinetics, namely in thermal oxidation the Si_2O_3 growing rate is lower than for native oxidized sample.

In Fig. 5 are presented the superimposed ARXPS normalized spectra for SO 00 sample after Ar^+ ion sputtering at U= 5 kV, t=10 min, I=100μA, and it is observed that the oxides are removed from the surface.(index for sample SO 01)

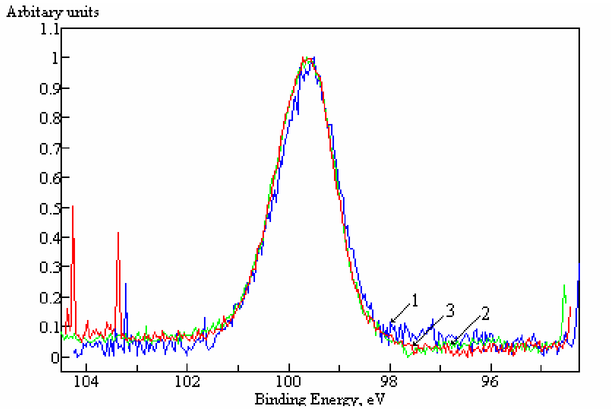

Fig. 5. Superimposed spectra for SO 01 sample for TOA: 25^0(blue), 55^0(green), 75^0(red) .

For silicon samples that are thermally oxidized at T=700^0C for t=5 hours in air is observed the growth of a thick layer of oxides and as a consequence in ARXPS spectra the signal for Si^0 is not observed on as received SO 10 and on SO 11 (exposed to ion sputtering at U=2 kV, t= 2 min, I=3μA), SO 12 (exposed to ion sputtering U= 2 kV, t=13 min, I=18 μA). For the SO 13 sample, exposed to Ar^+ ion sputtering in conditions U=2 kV, t= 30 min, I=18 μA, the signal of Si^0 appears well defined at TOA= 55^0 and TOA=75^0, as is presented in Fig. 6 for superimposed proportional spectra.

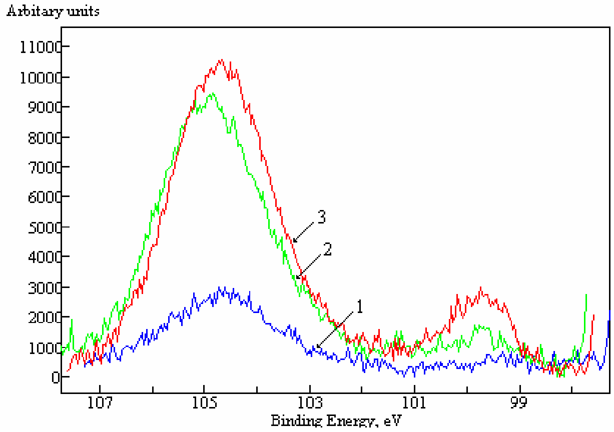

Fig.6. Superimposed spectra for SO 13 sample for TOA: 25^0(blue), 55^0(green), 75^0(red)

In Fig. 7 are presented the superimposed spectra for SO 10, SO 11, SO 12, SO 13 at TOA=75^0 and it is observed that with the increase of sputtering time it increases the full width at half maximum (FWHM) which means that the suboxides can be observed due to a preference in the oxides etching.

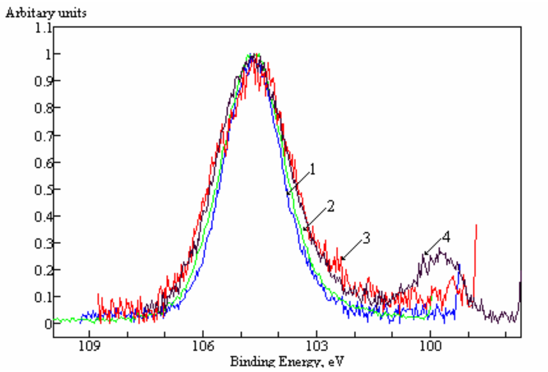

Fig.7.Superimposed spectra for SO 10 (blue), SO 11(green), SO 12 (red), So 13 (black) at TOA= 75^0

The ratio I_{oxy}/I_{Si} in the oxidation state Si^{4+} (SiO_2) can be evaluated for the sample SO 00, SO 13 and SO 20 and the computed values in accord with the presented theory lead to the following silicon dioxide layer thickness:

-d_{oxy} ~ 23.6 Å for native oxides on Si (SO 00 sample) and

- d_{oxy} ~ 27 Å for thermally oxidized ample (SO 20)

As observations we have: i)- in the characterization of native oxides layers and thermally oxidized layers in the ARXPS evaluation, the background was extracted from the measured Si 2p spectra and then the spectra were decomposed and ii)- the SiO_2 film thickness is larger in rapid oxidation (thermally grown) conditions with expected good accuracy.

4. Conclusions

There were studied the both oxides species grown on Silicon surfaces: exposed to natural oxidation process and also to air thermal oxidation in furnace at atmospheric pressure.

The XPS spectra for Si 2p lines were taken at the TOA: 25^0, 55^0 and 75^0. The deconvolution of the XPS lines has putted into evidence different oxidation states related to silicon dioxide (Si^{4+}-SiO_2) and suboxides as : Si^{3+} (Si_2O_3), Si^{2+}(SiO), Si^{1+}(Si_2O). The evolution of the suboxides lines at different TOA pointed out that the most sensitive angle to oxide structure is TOA=25^0 in the both cases of native oxidation and surface thermal oxidation. For native oxidized sample it prevails the suboxides species with high oxidation state (Si^{3+}) and for thermally oxidized samples it prevails the suboxides species with lower oxidation state (Si^{1+}) as a possible result of different oxidation kinetics. The position of BE for different oxidation states identified in our experiment are in a good agreement with the ones in literature.

The thickness of SiO_2 layer measured by ARXPS experiment and calculated in the condition of Electron Inelastic Mean Free Path (IMFP) as presented in literature since 1994 has the average values of d_{oxy}~23.6 Å for native SiO_2 and d_{oxy}~ 27 Å thermally grown SiO_2, respectively.

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