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Deconvoluted Si 2p Photoelectron Spectra of Ultra thin SiO_2 film with FitXPS method

A. Bahari *

Department of Physics, University of Mazandaran, Babolsar

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**Corresponding author:*
E-mail address:
a.bahari@umz.ac.ir

Abstract

The main impetus for our research is provided by the growing interest worldwide in ultra thin silicon dioxide on silicon based nano devices. The obvious need for better knowledge in the ultra thin gate silicon dioxides, is motivated both by interests in fundamental research and phenomenology as well as by interests in possible applications, which can be found with better fitting of experimental spectra. The up – and down- spin roles are considered for studying the nano structural properties of bulk, interface and surface states of ultra thin film, down to 2 nm and also appealing to the field of surface science. The obtained results show the above states can be determined and distinguished with spin orientations in FitXPS method.

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1. Introduction

The applied aspects of surface science play a major role in several technological areas such as micro electronics device technology, nanostructures and several more.

The spectroscopical surface techniques such as Synchrotron radiation for high resolution photoemission spectroscopy (HRPS), X-ray Photoelectron Spectroscopy (XPS) and Auger Electron Spectroscopy (AES) form a very broad class [1-5]. They are rightly considered routine tools for surface science and for many applications

in the development of advanced materials, devices and processes due to their high surface sensitivity, their capabilities of qualitative (both in terms of atoms and of their chemical situation) and quantitative analysis. They can be applied to real world samples as well as to model systems due to their relatively low destructive action on surface systems.

In these techniques, some kinds of energy distribution of particles emitted from the surface have been measured. It may be distributed over energies, angles, temperatures or other parameters and the particles may be incident particles that has been backscattered, or particles that has been ejected due to excitations in the surface region [2, 5-7]. The photoemitted intensity from each level j in HRPS is found the occupation number which is 2j+1. For the Si 2P peaks this gives a ratio of

$$\frac{Si\ 2\mathrm{P}_{1/2}}{Si\ 2\mathrm{P}_{3/2}} = \frac{2(1/2)+1}{2(3/2)+1} = \frac{1}{2}$$

Where j= L±S, L=1 and S=1/2. In this view, both XPS and HRSRS are used for the identification of elements present at a solid surface and offered precise measurements for ultra thin films, but are limited for thicker films due to the exponential decay functions that describe the sampling depth in both techniques.

However, this research has been done in the hope that it will be read by physicists, engineers and people working in areas related to ultra thin oxide, nitride and even high-k dielectric. One purpose has been to have the opportunity to learn about the remarkable area of experimental fitting processes for ultra thin systems on silicon as maybe the best material for gate dielectrics in future CMOS (complementary metal oxide semiconductor) generations [6-12]and another purpose is partly spawned by finding accurate sate positions and intensities. The FitXPS method in the present work helps us to separated bulk, interface and surface components with considering up- and down- spins.

2. Experimental procedures and details

The silicon sample (n-type, 5Ω-cm, 3cm × 1 cm) were cut out of wafers and introduced to the furnace after a rinse with ethanol and stone in an ultrasonic bath. After that they are immediately transferred inside the ultra high vacuum chamber where the base pressure was 10^{-11} Torr. All Si samples (3 cm x 1 cm in size) in XPS and HRPS were mounted on a holder with Ta- clips, which allows direct current heating. Practically, XPS experiments were performed with a SPECS PHOIBOS analyzer. This instrument is equipped with Al and Mg x -ray sources and concentric hemispherical analyzers.

Since these techniques involve the energy analysis of electrons emitted from the surface of a material by X-ray (photon), they can be inherently quantitative. It means that the intensities of the peaks which allow element identification are directly related to the atomic concentration within a sampled volume. Furthermore, important information about the chemical state of surface atoms can be obtained, particularly with XPS. In addition, Tanuma et al. [13] have reported IMFP (Inelastic Mean Free path) data for 50- 2000 eV electrons of 27 elemental solids and 15 inorganic compounds. For elements and inorganic compounds the scatter about a universal curve is least when the path lengths are expressed in monolayers. Analysis of the inter element and inter-compound effects [5, 7-17] shows a universal curve of the IMFP given by;

$$\lambda = \frac{1}{E^2} + \sqrt{a\ E}$$

Where $a = (A/\rho\, n)^{1/3}$ is the average monolayer thickness (nm) and E is the electron energy above the Fermi level in eV. A is the atomic or molecular weight of the material, ρ is density, and n is the number of atoms in the molecule. On the other hand, monochromatized photons, produced by suitable monochromators, and covering a wide range of energies, can be produced in this way.

As we know, when electrons in a synchrotron are accelerated, they radiate energy in the form of photons with an intensity maximum at a critical wavelength, (of order 0.1 - 0.4 nm, energy 1-10 KeV). Beam energies are several hundred MeV or higher and path radii many meters. The advantages of synchrotron radiation are the light photon intensity (orders of magnitude greater than characteristic X-ray sources at the same energies), the ability to tune (select or scan) the excitation energy and the fact that the radiation can be almost 100 percent plane polarized [15].

The photoemission experiments were carried out at the storage ring with the light from a bending magnet using a spherical grating monochromator and a SCIENTA analyzer with a diameter of 20 cm. The experimental chamber has two compartments separated by a valve to keep the analyses and beam line at the best possible vacuum, as the handing, heating and exposure of the samples is done in the other compartment. Clean and perfect Si(100)- 2x1 reconstructed surfaces were produced by heating to 10000 ^{o}C.

The exposure to oxygen is controlled via a calibrated inlet procedure, with gauges were in the chamber. The chamber was baked before the experiments.

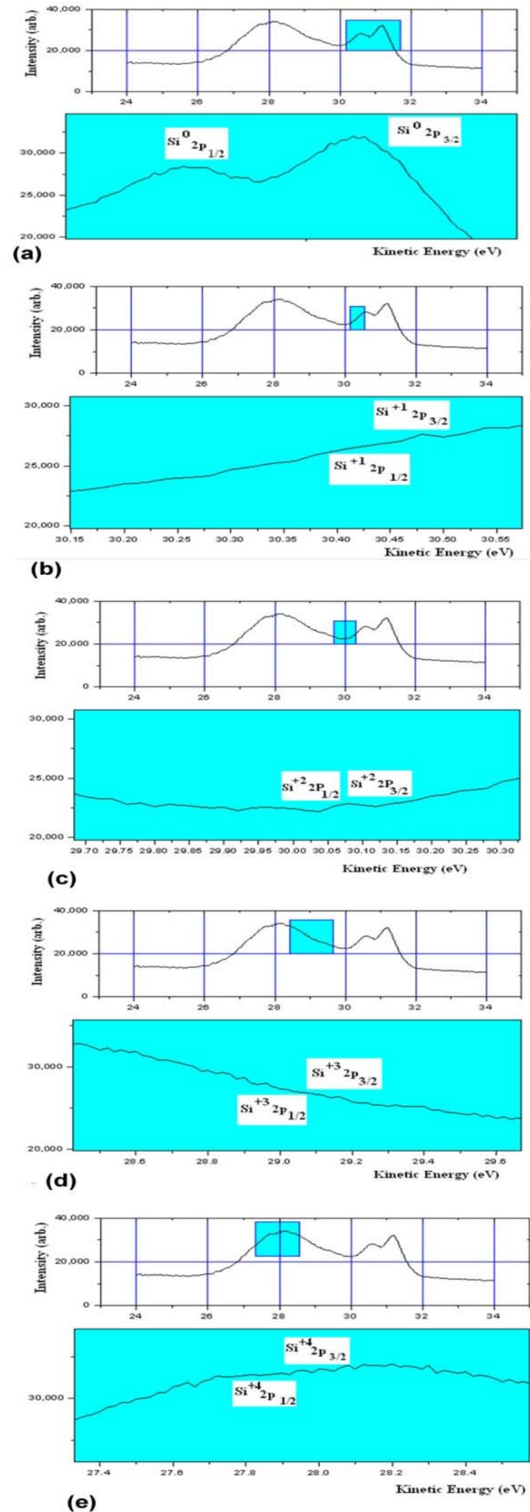

Fig. 1. Si 2p states of Si(100) spectra after exposure to 300- 2100L total oxygen at 500 ^{0}C: (a) Si $2p^{0}_{3/2}$, Si $2p^{0}_{1/2}$, (b) Si $2p^{+1}_{3/2}$, Si $2p^{+1}_{1/2}$, (c) Si $2p^{+2}_{3/2}$, Si $2p^{+2}_{1/2}$, (d) Si $2p^{+3}_{3/2}$, Si $2p^{+3}_{1/2}$ and (e) Si $2p^{+4}_{3/2}$, Si 2p+41/2.

The pressure was kept below 2 x 10^{-10} Torr at all times, except during the preparation of the sample. The incident angle of the light on the sample is 40 degrees from the normal. The temperature of the sample (above 4000 ^{o}C) was measured from outside the chamber by an optical pyrometer calibrated with respect to the sample and the transmission of the window of the UHV chamber. Keep in mind that for Si 2p, kinetic energy of electron is 24-34 eV , Ephoton = 131 eV, ΔE = 0.02 eV, Δt = 0.5 Sec, Slits: 50/50 and Epass = 20 eV.

Furthermore, since the intensity of the electron beam in the synchrotron drops over time, the intensity of the applied radiation drops as well, therefore, we here to normalize out the photon flux changes. The normalization was carried out by setting the average background level above (at higher kinetic energies). The spectra features to a constant level, equal to the lowest value average the set of spectra included in the experiment. We have used HRPS to study how silicon oxide onto Si(100) formed. The substrates are kept at a temperature of 5000 ^{o}C and 8000 ^{o}C.

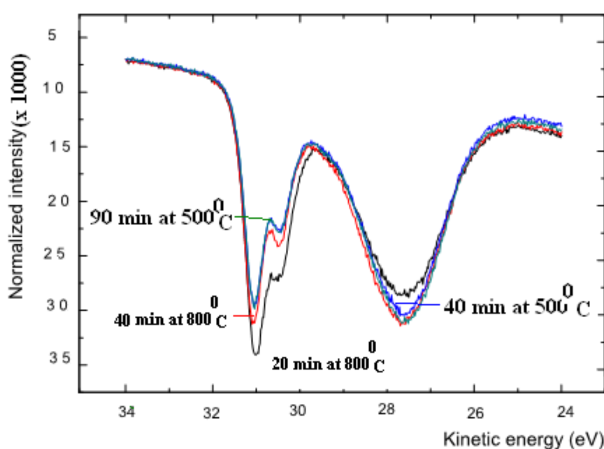

Fig 2: Si 2p spectra of Si(100) after exposure to 300-2100L total oxygen.

As shown in figures 1 and 2, after the first, short exposure, 300L O_2, the bulk Si 2p 3/2 and Si 2p 1/2 peaks are barely reduced in intensity but the surface peaks of the clean surface has disappeared, indicating a change of the surface reconstruction.

The following larger exposures change the structure of the entire spectrum (Fig. 2). The chemically shifted structures towards higher binding energies compared to the bulk peaks become more dominating due to the oxidation.

3. Fitting parameters of Si 2p (FitXPS)

In photoemission experiment a change of the binding energy results in a change in the opposite direction of the kinetic energy of the photoelectrons. In semiconductors with no surface bands crossing the Fermi level, one expects the single components to be convolutions of a Lorentz and a Gaussian, so called Voigt functions.

The Lorentzian width is correlated to the lifetime of the core- hole, denoted by LFWHM, of the Si 2p peak. Peak broadening due to transport, apparatus and temperature effects is expected to be Gaussian in nature and it is therefore obvious to start by keeping the Lorentzian width fixed in the fitting procedure (In the present work, LFWHM = 0.18).

Thus, the Gaussian width is determined by vibration and experimental broadening. It has been assumed that the Gaussian width is free but the same for both spin orbit components and that the asymmetry parameter is zero (see table). The remaining of the parameters is all free. Since a direct scaling of the background to precisely fit the background in the spectrum is not possible, a linear/parabolic background has been added as a compromise. The surface sensitive Si 2p spectra are usually recorded using 131 eV photons. As

seen from the IMFP figure in [16], photoelectrons with energy of some 30 eV have the lower mean free path possible.

There are also some quantities such as the atomic photoionization cross sections ($\sigma_{SiO_2}/\sigma_{Si}=2.2$) [17] at 131 eV, the escape depths, and the density of Si atoms which should be considered in the analysis. In the case of oxide film thicknesses smaller than 0.5 nm, the spectra are studied with appropriate line widths, the intensity ratio and energy resolution. Such detailed analysis is quite important in determining small chemical changes in the initial stage of oxidation. The fitted parameters include almost the same widths of a given peak as parameters of all fits, and only energies and relative intensities are allowed to vary. However, for the final agreement also some small relative changes of the energy differences between the bulk- Si and the shifted peaks are allowed. The asymmetry parameter is set zero because Si is not a metal and hence the spectra are not asymmetric. The GFWHM of two spin- orbit coupled peaks is required to be equal since both peaks are from the same chemical environment and will have the same thermal broadening. The structural issues are thus reflected in the deconvoluted spectra: the clean surface spectra contain components related to surface atoms and bulk atoms. The surface atoms give rise to peaks, which are shifted and broadened compared to bulk atom peaks. Generally, after removing the background [18], the spectrum is decomposed into Si 2p 1/2 and Si 2p 3/2 spin-orbit partner lines. This decomposition is mathematically unique as long as the spin- orbit splitting and the intensity ratio are known.

The splitting of 0.61 eV is an atomic property and is practically independent of the chemical environment. A variation of the splitting between 0.59 and 0.61 eV has been observed by fitting the bulk lines [19]. The 2p 1/2 to 2p 3/2 intensity ratio comes out in these fits to be equal to the statistical value of 1:2 within 2 percent. Results obtained from FitXPS fitting for 40 min at 5000 C and at 8000 C (Figure 3) demonstrated that the oxide thickness and bulk area have been decreased which confirmed the XPS results (see table 1 and [2-4]).

Therefore, as many workers [5, 17, 20] suggested in the near- interface region there is a zone with excess Si in the SiO_2 region. From the view of technique point, for instance, from ellipsometery measurements, the interface region is understood as a layer with optical properties different from both bulk oxide and crystalline silicon, although how is not very clear.

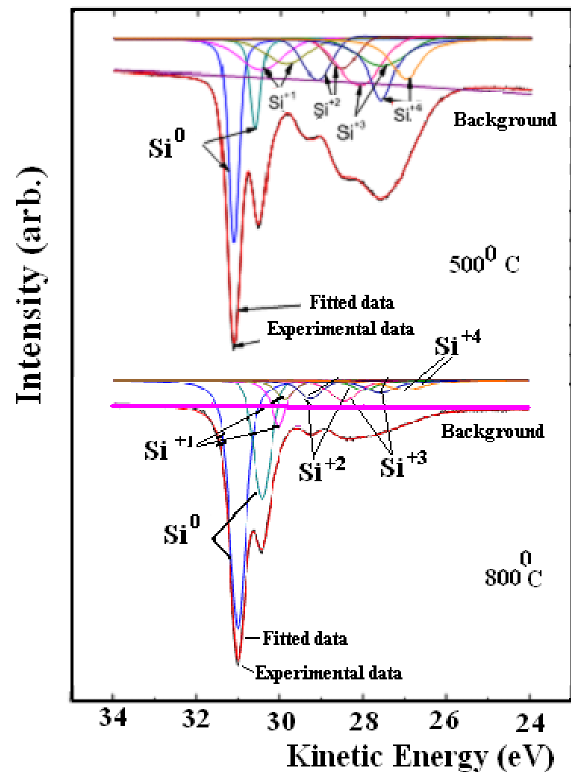

Fig. 3. Fit of Si 2p spectrum of Si (100)- 2x1 exposed to 40 min O_2 at 500 ^{0}C (up) and 800 ^{0}C (down).

Table 1. Fitting parameters for the spectrum of SiO2/ Si(100) after exposure 90 min at 5000C and 20 min at 8000C.

Component $Si\,2P_y^z$	-0.01 (Δ E_{Pass} ± 1 (eV))	he height f Peak	The area under Peak	0.01 (GFWHM ± 1)
500^0 C y = 3/2, z = 0	0	86110	36660	31
800^0 C y = 3/2, z = 0	0	34210	18500	23
500^0 C y = 1/2, z = 0	59	8773	18080	31
800^0 C y = 1/2, z = 0	48	8102	8790	23
500^0 C y = 3/2, z = +1	76	27630	24390	18
800^0 C y = 3/2, z = +1	60	12280	3951	36
500^0 C y = 1/2, z = +1	140	37920	12181	18
800^0 C y = 1/2, z = +1	120	1674	2000	36
500^0 C y = 3/2, z = +2	189	11470	5533	66
800^0 C y = 3/2, z = +2	152	1006	1109	20
500^0 C y = 1/2, z = +2	244	20590	2800	66
800^0 C y = 1/2, z = +2	193	1936	5600	20
500^0 C y = 3/2, z = +3	306	66000	14930	87
800^0 C y = 3/2, z = +3	263	1680	2677	98
500^0 C y = 1/2, z = +3	355	57000	7501	87
800^0 C y = 1/2, z = +3	315	1493	1300	98
500^0 C y = 3/2, z = +4	360	49000	13030	97
800^0 C y = 3/2, z = +4	362	1493	1677	75
500^0 C y = 1/2, z = +4	415	23910	6500	97
800^0 C y = 1/2, z = +4	403	1320	840	75

The interpretation of the Si 2p photoemission consider this region as a layer of Si^{+n} suboxide states (such as Si^{+2} from SiO) [17] with local electronic configurations different from pure Si and bulk SiO_2 [21].

We face two problems: The refractive index of thin films ellipsometery and other optical techniques) and the photoelectron mean free path (photoemission) which are not universally agreed upon, which change as the composition of this region changes [22, 23].

Photoemission experiments provide evidence of Si atoms that are bonded to one, two, or three O atoms, the rest of the neighbors in each case being Si atoms. A totally abrupt (100) interface would have only a single plane of Si^{+2} atoms and no Si^{+1} or Si^{+3} [24]. The presence of the latter is equivalent to suboxide bonds (Si- Si bonds on the oxide side). But, figures 1 and 2 show that it could be an even more challenging problem to achieve a totally abrupt interface.

Pantelides and Ramamoorthly [25] suggested that the amorphous nature of the oxide allows enough flexibility to avoid point defects, but oxidation is known to be accompanied by emission of Si interstitials. Such excess interstitials have been detected in the Si substrate by their effect on oxygen and by the growth of oxide. The common wisdom is that emission of Si atoms, which is required by volumetric forces must require the breaking of bonds and thus dangling bonds ought to be a frequent by product. The case of forming Si^{+1}, is thought as the insertion of an oxygen atom between two Si atoms consisting of a Si-Si bond oriented along the Si directions, while in the case of forming Si^{+3}, the insertion of an oxygen atom is between two Si atoms consisting of a Si-Si bond at the interface expanding the oxide network mostly along the direction perpendicular to substrate

direction [5]. Therefore, the formation of Si+1 at the interface results in an increase in surface roughness caused by the formation of protrusions on the oxide surface. Thus, the saturated level of intermediate oxidations states is slightly larger. Furthermore, the relative number of intermediate oxidation states does not change significantly upon increasing the oxidation temperature.

4. Conclusions

The interface and near interface regions of Si/SiO2 and related films have received intensive scrutiny for several decades.

Nevertheless, the origin of interface states has been based on the assumptions of unsaturated dangling bonds at the interface. In addition to the free dangling bonds, silicon and oxygen bonds in the oxide are distorted at the interface to match the silicon lattice. In the Chemist's language: near the interface, Si is Si^{+4} as in SiO_2, at the interface Si is also found in its Si^{+1}, Si^{+2} and Si^{+3} states.

However, as found in fitting program, the interface region width depends not only on the substrate and oxide layer fabrication procedure, but also on the measurement techniques used. FitXPS method for Si oxygen transports into silicon shows the formation of bonds which indicate that within the fit monolayer there are extra silicon atoms due to stress, before oxygen goes into the silicon network.

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References

[1] S. G. Pandalai, Recent research developments in Applied physics, Transworld research network, 2002.

[2] P. Morgen, A. Bahari, and K. Pedersen, Characterization of Nano scale materials: Nano structured, Springer, 2006.

[3] A. Bahari et al., Physical Review B ., 72 (2005) 205323.

[4] P. Morgen et al., Journal Vacuum and Technology A, 23 (2005) 201.

[5] Y. J. Chabal, Fundamental Aspects of silicon oxidation, Springer, Springer- New York, 2001.

[6] A. Bahari et al., Surface Science, 600 (2006) 2335.

[7] A. Bahari et al., Journal Vacuum, Science and Technology B, 24 (2006) 2119.

[8] A. Bahari , Acta Physica Polonica, 115 (2009) 622.

[9] A. Pasquarello et al., Nature, 396 (1998) 58.

[10] K. Hirose et al., Physical Review B ., 59 (1997) 5617.

[11] A. Pasquarello, Microelectronic Engi., 48 (2011) 89.

[12] A. Bahari et al., Surface Science, 602 (2008) 2315.

[13] S. Tanuma et al., Surface and Interface Analysis, 21 (1994) 165.

[14] M. P. Seah and W. A. Dench, Surface and Interface Analysis, 1 (2007) 2.

[15] A. Bahari and M. Amiri , Acta Physica Polonica, 115 (2009) 625.

[16] P. Morgen, Computational Materials Science, 21 (2001) 481.

[17] F. J. Himpsel et al., Physical Review B . 38 (1988) 6084.

[18] S. Tougaard, Journal Vacuum, Science and Technology A, 14 (2009) 1415.

[19] D. Adams and J. N. Andersen, FITXPS: a fitting program for core level spectra available from; ftp: //boobpic. ifa. au. dk/pub/ fitxps.

[20] I. J. R. Baumvol, Surface Science Report, 36 (1999) 1.

[21] Dimitrijer and Harrison, Journal of Applied Physics, 80 (1996) 2467.

[22] S. Y. Kim and E. A. Irene, Review of Scientific Instruments, 66 (1995) 5277.

[23] J. W. Kim and H. W. Yeom, Physical Review B ., 67 (2003) 035304.

[24] S. M. Sze, Semiconductor device physics and technology, Wiley, New York, (1985).

[25] M. Ramamoorthly and S. T. Pantelides, Applied Physical Letter,75 (2009) 115.