Determination of inelastic mean free paths of high kinetic energy electrons (>6 keV) in oxides. Attenuation lengths of high energy photoelectrons in compact and mesoporous SiO_2 films

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Hard x-ray photoemission spectroscopy (HAXPES) is getting an increasing interest because it allows studying thicker and/or buried layers (up to few tens of nm) than traditional XPS, keeping the chemical sensitivity. In HAXPES, monochromatic hard X-rays are used as excitation source (photon energies > 3 keV), so high kinetic energies photoelectrons are excited. For elemental quantification purposes, reliable attenuation lengths (AL) or IMFP for high kinetic energy electrons have to be used. Although extrapolation of well-established formulae can be used, there is a strong interest in the experimental evaluation of these quantities to validate (or not) the proposed formulae. This is of special interest when we deal with mesoporous materials, i.e., materials with pores sizes smaller than the expected IMFP for high energy photoelectrons.

Well characterized compact and porous SiO_2 thin films samples were deposited on polished Si(100) wafers. The compact SiO_2 thin films were produced by reactive magnetron sputtering and the porous SiO_2 films (55% of compact SiO_2 and 45% of voids) were prepared by electron beam evaporation with glancing angle deposition (GLAD) configuration. No cleaning procedure was used before their HAXPES characterization. HAXPES analyses were performed using a high energy FOCUS electron spectrometer [1]. Photon energies of about 10.0, 12.5 and 15.0 keV were used to excite Si 1s signal of the samples (from the SiO_2 films and the Si substrate). The energy resolution $\Delta E/E$ of the beamline was 1.5×10^{-4}. Si 1s photoemitted electrons of about 8.2, 10.7 and 13.2 keV were recorded with spectrometer energy resolution of 1 eV. The acceptance angle during HAXPES acquisition was $\pm5^{o}$. The angle of incidence α of the radiation was 85^{o} with respect to the surface normal and the emission angle θ was 15^{o} off normal. The beam size was about 0.5x0.5 mm^2 and the number of photons at the sample was about 2×10^{11} ph/s. X-ray reflectometry (XRR) measurements were performed in situ (at the same vacuum chamber that the HAXPES measurements) to characterize the thickness and roughness of the SiO_2 films at exactly the same sample position where the HAXPES characterization was made.

Evaluation of the ALs was done using the two-peak overlayer method that applies to the determination of SiO_2 thickness on Si wafers as described by Seah et al. in a series of papers [2]. According to these authors, ALs can be obtained from the expression

$$AL(E) = d / (\cos\theta \cdot \ln (1+(R_{expt}(E)/R_0))) \qquad (1)$$

where $R_{expt}(E)$ is the I_{Si}^{4+}/I_{Si}^{0} intensity ratio of the Si 1s signals from the SiO_2 layer and the Si substrate in the HAXPES spectra, and R_0 is the equivalent ratio of intensities, $I_{0,Si}^{4+}$ and $I_{0,Si}^{0}$, from bulk oxide and substrate, respectively. R_0 can be evaluated theoretically [3] according to

$$R_0 \approx 0.20 \cdot \rho_{SiO2} \cdot (\lambda_{SiO2}/\lambda_{Si}) \qquad (2)$$

where ρ_{SiO2} is the density (gr/cm^3) of the SiO_2 film (evaluated from optical measurements in this work). $\lambda_{SiO2}/\lambda_{Si}$ corresponds to the ratio of the inelastic mean free path for electrons travelling in the SiO_2 overlayer and Si substrate. To a good approximation this ratio is a constant, that according to TPP2M gets the values 1.26 and 1.50 for the compact and porous SiO_2, respectively. Thus, the theoretical values of R_0 in eqn.(2) are 0.53 and 0.36 for the compact and porous SiO_2. At this point it is worth mentioning that the use of R_0 = 0.93 has been recommended in the past [2,3] for compact SiO_2 based on standard XPS measurements. This was mainly justified as a relative lack of intensity at the Si 1s peak of the metallic state compared to the oxide state due to the corresponding uneven contribution of shake-ups at the first plasmon excitation.

Figure 1a shows HAXPES Si 1s spectra (raw data) corresponding to a porous (left) and compact (right) SiO_2 samples acquired using 10.0, 12.5 and 15.0 keV photon energies. The characteristic Si^{4+} and Si^{0} signal from the SiO_2 layer and Si substrate are clearly identified. Besides, the Drude plasmon excited at the Si substrate is also clearly visible at 17.2 ± 0.1 eV lower kinetic energies than the Si^{0} signal. Bulk plasmon in Si^{0} is reported with 16.8 eV energy loss both from reflection electron energy loss [4] and standard photoemission experiments [5]. The difference (about 0.4 eV) can be ascribed to recoil effect due to the high energy of the emitted electrons, in agreement with theoretical predictions [6].

Figure 1b depicts the calculated experimental AL values for the compact (full symbols; circles, squares) and porous (hollow symbols) SiO_2 films, evaluated from the quantification of the measured Si 1s spectra of the SiO_2 thin films according to eqn(1) and the theoretical R_0 according to eqn(2). Figure 1b also includes the evaluation of AL for the compact (full stars) and porous (hollow stars) SiO_2 samples considering R_0 = 0.93. These AL are about the largest (between 15 and 35 nm) experimental AL values ever reported for photoelectrons with kinetic energies in the 8-13 keV. This figure also includes theoretical IMFP obtained from extrapolation for high kinetic energies of the TPP2M formula [7] for the compact (full line) and porous (dashed line) SiO_2 films considered in this work.

The experimental AL values obtained for the compact SiO_2 samples, are ~10% lower (R_0=0.53) or ~17% higher (R_0=0.93) than the prediction of the TPP2M formula. In case of porous SiO_2 samples the experimental AL values are

~4% lower (R_0=0.36) or ~58% higher (R_0=0.93) than prediction. Note that for the kinetic energies considered in this work, IMFP and AL differ less than 2% from each other [3]. The data in Figure 1b are presented in log-log scale to stress the power law dependence on kinetic energy of AL (i.e., AL, IMFP $\propto E^m$, where the exponent m corresponds to the slope of the corresponding least squared fit). We obtain that the m values for the experimental observations are 0.81 $\pm$ 0.13 and 0.72 $\pm$ 0.12 for compact and porous materials, respectively. These values are slightly lower than m=0.86, the value predicted by the TPP2M formula for these films.

We have observed that by incorporating ~45% voids in a mesoporous structure to SiO_2, the IMFP increases by ~24% with respect to that of the compact SiO_2 material if theoretical R_0 values are considered. This result is in reasonable agreement with the predictions of TPP2M (a ~20% increase). Besides the absolute AL values obtained for the compact SiO_2 samples, are close to those predicted by TPP2M formula (~10% and ~4% lower than the prediction for compact and porous SiO_2 films, respectively).

Considering these results and that in previous studies was found reasonable agreement between experimental finding of AL [8] and TPP2M predictions of compact SiO_2, the results reported in Figure 1b indicate that the use of TPP2M formulae can safely be extrapolated not only to high kinetic electron energies (up to 13 keV) but also to micro-mesoporous materials with same chemistry but different density. This is an important result because it constitutes the first experimental evidence of the validity of TPP2M for mesoporous materials.

Relative to the excitation of surface plasmons by the high energy photoelectrons, the presence of extra surface losses [9] due to the multiple crossing of the electrons through the mesoporous structure (note that the AL in this case are significantly larger than the pore size) would tend to decrease the observed AL with respect to that predicted by IMFP predictive formulae that in general do not include surface losses. This effect would decrease the difference between AL from compact and porous films. Experimentally we observe the opposite behavior (AL of the porous SiO_2 samples increase by ~24% with respect to that of the compact SiO_2 material while the TPP2M formula predicts a ~20% increase), so we may conclude that surface effects do not seem to be major contribution to the AL, despite the fact that the photoelectrons travel through a series of vacuum-solid interfaces due to the mesoporous nature of the films.

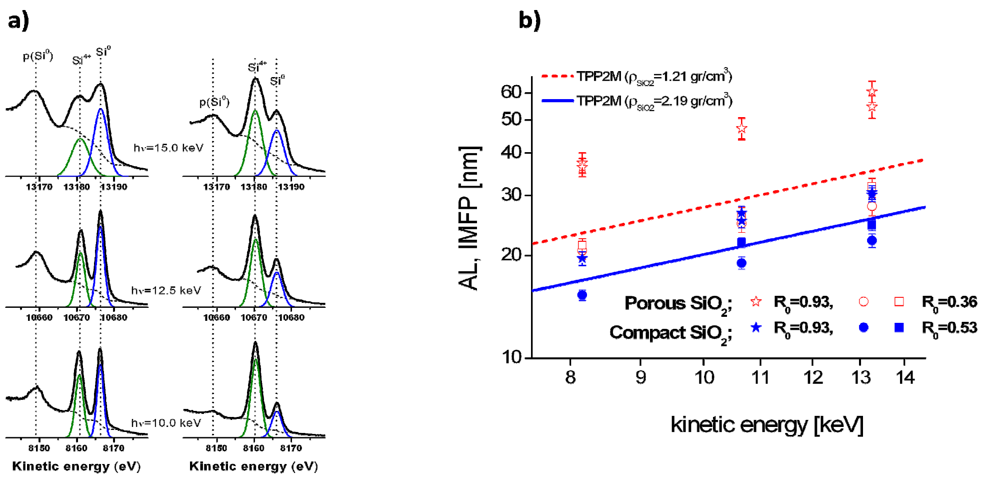

Figure 1a. Si 1s spectra acquired with 15.0 (top), 12.5 (middle) and 10.0 keV (bottom) photon energies of a porous (left) and compact (right) SiO_2 sample deposited on Si(100) wafers.

Figure 1b. Attenuation lengths (AL) obtained after analysis with the two peaks overlayer method of the HAXPES measurements on compact (full symbols) and porous (hollow symbols) SiO_2 films (see text). The errorbars correspond to assume an uncertainty of ±10% in the R_0 values. Full line (dash line) corresponds to the prediction of the extrapolated IMFP values of TPP2M formula for compact (porous) SiO_2.

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