



XPS measurements for probing dynamics of charging

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ABSTRACT

The technique of recording X-ray photoemission data while the sample rod is subjected to ± 10.0 V (dc) or square-wave pulses (ac) with varying frequencies in the range of 10^{-3} to 10^3 Hz for probing charging/discharging dynamics of dielectric materials, is reviewed. Application of this technique introduces charging shifts as well as broadening of the peaks, which depend non-linearly on the polarity, as well as on the frequency of the pulses applied. These changes have been measured on: (i) an artificially created dielectric sample consisting of a Au metal strip connected externally to a series resistor of $1\text{ M}\Omega$ and a parallel capacitor of 56 nF , and two real dielectric films; (ii) a 20 nm organic polystyrene film spin-coated on a silicon substrate; (iii) a 10 nm SiO_2 inorganic layer thermally grown on silicon. A simple circuit model is introduced to simulate the charging shifts and the peak broadenings. Although this simple model faithfully reproduces the charging shifts in all three cases, and also some of the broadenings for the artificial dielectric and the polystyrene film, the additional broadening in the negatively charged peaks of the SiO_2 dielectric film cannot be accounted for. It is also claimed that these experimental findings can be used for extracting material-specific dielectric properties.

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1. Introduction

Control of charge accumulation and dissipation (charging/discharging) in dielectric materials is the essence of the rational design of various devices and sensors [1]. This is especially important for SiO_2 as the thickness of the dielectric layer is expected to shrink down to few atomic layers for the next generation of metal-oxide-semiconductor (MOS) devices [2]. On the other hand, organic dielectric materials, are also important class of materials utilized for various applications, and here again, charge accumulation/dissipation is pivotal for their advanced functionalities [3–5]. Accumulation of charge in a dielectric layer occurs via various trapping mechanism(s) and is normally probed by electrical current–voltage and/or current–capacitance measurements [6–9]. Photoemission, utilizing UV, X-rays and lasers, has also been employed for probing very fast ($<10^{-9}$ s) charging dynamics [10–12]. Core-level X-ray photoemission, XPS, is especially attractive since additional chemical information can also be derived from the line positions of the corresponding peaks. However, the measured line positions are altered by local potentials developed, due to the uncompensated charges resulting from photoelectron emission, especially for poorly conducting samples or regions (layers or

domains) within such samples [13–19]. Excellent charge compensation methods have been developed using low-energy electrons, ions and/or photons [20,21].

One can also utilize XPS for understanding the mechanisms leading to and/or controlling of the charging/discharging processes in materials, which offer great possibilities for researchers in all fields [22]. Several applications have been reported, utilizing the charging, called controlled surface charging, for extracting chemical, physical, structural, and electrical parameters of various surface species [23–28]. For example, it was shown that monolayer films are not affected, but multilayer films are affected by the voltage applied [29,30]. Recently, using silica-coated gold substrates secondary electron emission control in XPS has been shown by employing sample biasing and a top retarding grid to control the photoelectron current [31]. Islam and Mukherjee have used the positive charging to derive information about the structure of Langmuir–Blodgett films of cadmium arachidate on silicon substrate [32]. Using a slightly different strategy, and by applying voltage stress to the sample while recording XPS spectra, we have shown that the extent of charging can be controlled via which a range of analytical and electrical information could be extracted [33–36]. In addition to static information derived from application of dc voltage stress, dynamical information can also be extracted if the voltage stimuli is applied in the form of pulses, as we have recently reported [37–42].

In this contribution, we review our recent investigations for analysis of XPS data, recorded by applying the voltage stress in the form of bipolar square-wave (SQW) pulses for probing

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charging/discharging dynamics of thin dielectric surface structures, and we also supplement our experimental data with a theoretical model. Previously reported dynamical photoemission measurements have been either in the ultra-fast, sub-pico-seconds regime using laser excitations [10–12], or in a much longer time regimes (10^1 to 10^4 min) with conventional XPS measurements [17,24,43–45]. Our measurements fill this gap and provide information on charging/discharging dynamics of dielectric materials in the range of 10^{-3} to 10^3 s, matching those of many chemical–biochemical processes [46].

2. Experimental

For the case of inorganic dielectric material we have chosen a ca. 10 nm silicon oxide layer grown thermally on HF-cleaned Si (1 0 0) substrates at 500°C in air. For organic dielectric we have used a thin film (20–60 nm thick) of polystyrene (PS) spin-coated on a clean silicon substrate from a solution in chlorobenzene. Chlorobenzene is chosen since it is known not to have a strong influence on the surface composition [47]. Average thicknesses of the films are measured using a stylus profilometer. A Kratos ES300 electron spectrometer with Mg K α X-rays (nonmonochromatic) is used for XPS analysis. A typical sample is a ca. 0.5 mm-thick silicon wafer with dimensions of 4 mm \times 12 mm. In the standard geometry the sample accepts X-rays at 45° and emits photoelectrons at 90° with respect to its surface plane. The sample can also be rotated to decrease the emission angle (electron take-off angle) in order to enhance surface sensitivity while keeping the X-ray-sample-analyzer angle always at 45° . Calibration of the energy scale was carried out using standard silver and gold samples and referencing to the C 1s peak at 285.0 eV. Resolution of the spectrometer was better than 0.9 eV measured in the Ag 3d peaks and we used standard curve fitting routines with 0.6 eV spin-orbit parameter for the Si 2p peak.

For probing charging or electrical properties, the sample substrate is subjected either to ± 10 V dc stress or to SQW of ± 10 V amplitude with varying frequencies in the 10^{-3} to 10^3 Hz range, while recording XPS data.

Samples are electrically connected both from the top (the oxide layer or the polymer film) and also from the bottom (the silicon substrate) to the sample holder, which is electrically isolated from the spectrometer ground, through which the external voltage stress can be applied. For controlling the charging state of the sample via the applied external voltage stress, a simple hot tungsten filament is placed near the sample. Typically 3.0 A current is passed from the filament, which is kept ca. -2 V with respect to the ground. Typical currents are ca. 10 nA due to photoelectrons going out of the sample into the spectrometer, and ca. 20 nA going into the spectrometer from the X-ray gun and/or stray electrons from the other features like ion-gauge, etc. However, the largest supply of electrons is the filament where the currents as high as $10\ \mu\text{A}$ can be obtained when the sample is positively biased [38,39].

3. Results

3.1. Control of charging/discharging properties by application of dc stress

When an external voltage stress is applied to the sample substrate, while recording an XPS spectrum of a poorly conducting/dielectric material, the binding energies shift in a very non-linear fashion due to variation of the electron current passing through the sample. This is best exemplified by measurements carried out on a very thin SiO_2 overlayer (<10 nm), since the Si 2p peaks of both the oxide and the silicon underlayer can be observed simultaneously as shown in Fig. 1 for a sample with ca. 5 nm oxide

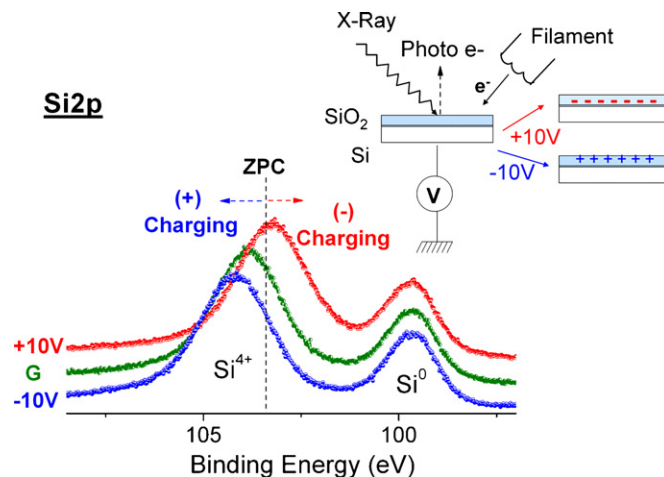


Fig. 1. Si 2p region of the XPS spectrum of a silicon wafer sample containing ca. 5 nm thermal oxide layer when the sample is grounded and under +10 and -10 V external bias, and when it is subjected to additional low-energy electrons from a filament nearby. The inset on the top right depicts the experimental setup.

thickness. As can be seen from the figure the changes in the measured positions of the Si 2p peaks as a function of the applied potential to the sample of silicon are very different with respect to the polarity of the voltage stress. After correcting for the simple potential shifts, the peak of the underlying substrate (Si^0) aligns perfectly, however, the peak of the oxide layer (Si^{4+}) shifts non-linearly, leading to different measured chemical shifts due to the differences in the electrical potential built-up as a result of charging. The Si 2p binding energies of the substrate and a truly uncharged oxide layer (at the zero-point-charge state, ZPC) are 99.5 and 103.2 eV, respectively [24]. Hence, a measured binding energy larger than 103.2 eV corresponds to a positively charged oxide layer, and a smaller value is the sign of a negatively charged oxide layer. Accordingly, as shown in Fig. 1, both in the cases where the sample is grounded and when a -10 V potential is applied externally, the oxide layer is positively charged, due to the uncompensated photoelectrons leaving the sample. Only after application of $+10$ V, the oxide layer becomes negatively charged due to a relatively larger electron current flowing through the sample, since more electrons from the filament are attracted to the positively biased sample. As we had shown in our previous time-dependent XPS measurements, the charging state of the oxide layer can easily be controlled by changing the polarity of the external bias, and the fully charged (or discharged) state in the oxide layer is achieved within few seconds [36,38].

3.2. An artificial dielectric layer: Au (m) + external RC

The simplest model system for relating the experimentally measured charging shifts in the binding energies (BE), and equally important, in the full-widths-at-half maximum (FWHM) of the corresponding peaks, to the charging/discharging capacities, and/or electrical properties of the dielectric sample(s) under consideration, might be considered as the dielectric layer having a series resistance (R) and a parallel capacitance (C). For that reason, we first took a Au metal strip and measured both the BE and the FWHM of the Au 4f spin-orbit doublet, under different experimental conditions as shown in Figs. 2 and 3. First type of measurements involve application of -10 and $+10$ V dc to the sample, which simply shifts the Au 4f position at 84.0 eV to higher and lower 10.0 eV values exactly, since the gold metal is perfectly conducting. However, the shifts are quite asymmetrical when an external series resistance of $1.0\ \text{M}\Omega$ value is incorporated into the circuit. Although no significant shift is observed in the case where -10 V applied, since

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