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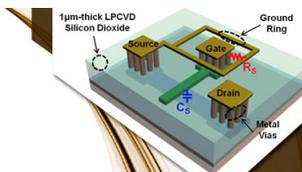
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X-ray photoelectron spectroscopy for resistance-capacitance measurements of surface structures

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In x-ray photoemission measurements, differential charging causes the measured binding energy difference between the Si $2p$ of the oxide and the silicon substrate to vary nonlinearly as a function of the applied external dc voltage stress, which controls the low-energy electrons going into and out of the sample. This nonlinear variation is similar to the system where a gold metal strip is connected to the same voltage stress through an external 10 Mohm series resistor and determined again by x-ray photoelectron spectroscopy (XPS). We utilize this functional resemblance to determine the resistance of the 4 nm SiO₂ layer on a silicon substrate as 8 Mohm. In addition, by performing time-dependent XPS measurements (achieved by pulsing the voltage stress), we determine the time constant for charging/discharging of the same system as 2.0 s. Using an equivalent circuit, consisting of a gold metal strip connected through a 10 Mohm series resistor and a 56 nF parallel capacitor, and performing time-dependent XPS measurements, we also determine the time constant as 0.50 s in agreement with the expected value (0.56 s). Using this time constant and the resistance (8.0 Mohm), we can determine the capacitance of the 4 nm SiO₂ layer as 250 nF in excellent agreement with the calculated value. Hence, by application of external dc and pulsed voltage stresses, an x-ray photoelectron spectrometer is turned into a tool for extracting electrical parameters of surface structures in a noncontact fashion. © 2005 American Institute of Physics. [DOI: 10.1063/1.1919396]

X-ray photoelectron spectroscopy (XPS) is a powerful analytical technique for deriving chemical and physical information about 0–20 nm surface structures. Its power stems mostly from its ability in resolving the chemical identity of the atoms from the measured binding energies.¹ Although the photoelectron emission is a weak process, a finite, measurable, and more or less steady current (0.1–20 nA) flows from the sample, which usually causes unwanted positive charging in poorly conducting samples or parts of surface heterostructures.² The positive charging is usually compensated for by a directed flow of low-energy electrons (or ions) from an external unit (flood-gun) to the sample, which under certain circumstances, overneutralizes it and can even cause negative charging. This negative charging, dubbed as controlled surface charging, has been utilized for deriving some chemical/physical parameters of surface structures.^{3–6} Otherwise, the emphasis, until now, has mostly been on recording the line positions in XPS, and except for very few cases,^{7–11} no attempts for electrical measurements have been made. The total current is the sum of two opposing currents, resulting from photoelectrons, and secondary electrons going out of the sample, and stray electrons or electrons from the flood gun, going into the sample, which can easily be controlled by application of a small (0–10 V) external bias, as we have

reported recently.^{12,13} In this contribution, we extend our application and report simple and noncontact electrical measurements derived from XPS data.

SiO₂ layers were grown thermally on HF-cleaned Si (100) substrates at 500 °C in air. Thickness of the overlayers was estimated from their angular dependency.¹⁴ A Kratos ES300 electron spectrometer with Mg K α x rays (nonmonochromatic) was used for XPS measurements. In the standard geometry, the sample accepts x rays at 45° and photoelectrons at 90° with respect to its surface plane are analyzed. Samples were electrically connected both from the top (oxide layer) and the bottom (silicon substrate) to the sample holder, which was grounded or biased with a dc power supply externally. For electrical measurements, a gold metal strip was also connected to the sample, and a series resistor (0.1–20 Mohm) and/or a parallel capacitor (0.1–1000 nF) were connected externally. Resolution of our spectrometer is slightly better than 0.80 eV as measured in the Ag 3d peaks and we use standard curve fitting routines with 0.60 eV spin-orbit parameter for the Si $2p$. Since we extract binding energy differences by fitting the entire silicon substrate and the oxide peak, we estimate our error in measuring the binding energy differences to be better than 0.05 eV. For time resolved measurements, the bias was stepped and pulsed. During each pulse 200 measurements with 5 ms (or larger) resolution were recorded, the voltage was stepped and pulsed for the next 200 measurements until a region was completed.

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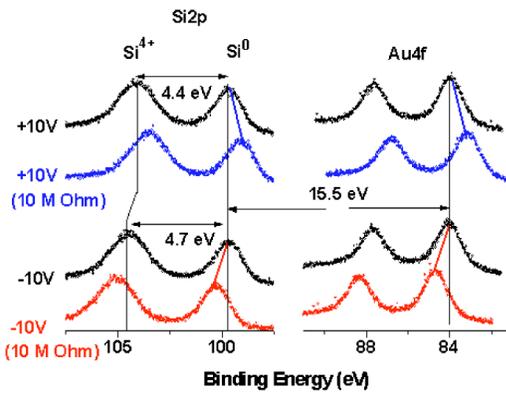


FIG. 1. (Color online) XPS spectra of the Si 2*p* and Au 4*f* regions of a silicon substrate having ~ 4 nm oxide layer, and in electrical contact with a gold metal strip, under +10 V and -10 V external bias, and also without and with a 10 Mohm series external resistor. The voltage bias affects the measured binding energy difference between the silicon oxide and the silicon substrate peaks and introduction of an external resistor induces an increase in the kinetic energy of all peaks under positive bias and decreases under negative one.

Several scans were implemented for signal averaging.¹⁵

When an external voltage stress is applied to the sample rod, while recording the XPS spectrum, the binding energies shift in a very nonlinear fashion due to variation of the electron current passing through the sample. Figure 1 shows the Si 2*p* and Au 4*f* peaks of a ~ 4 nm thick SiO₂/Si system tied together with a gold metal strip under [Fig. 1(a)] +10 and [Fig. 1(b)] -10 V bias, where approximately a 0.3 eV difference develops between the Si⁴⁺ and Si⁰ peaks with no measurable difference between the Si⁰ and Au 4*f* peaks. When this difference is plotted against the external voltage, an S type of a curve is obtained as shown in Fig. 2.

In order to quantify the current, and establish an equivalent circuit, we have incorporated an external 10 Mohm resistor into the system which shifts all the peaks toward a higher kinetic energy (blueshift) at positive bias and a lower kinetic energy (redshift) at negative bias as also shown in

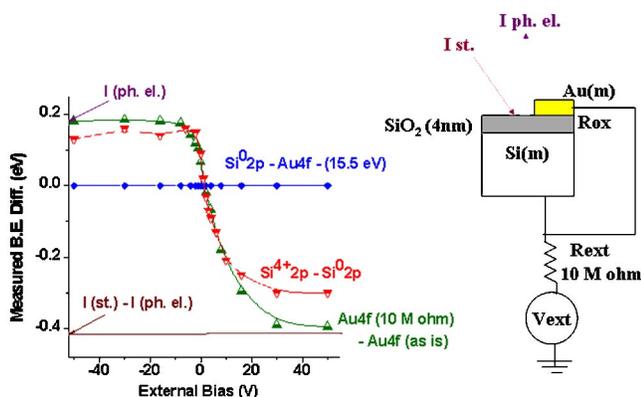


FIG. 2. (Color online) The measured binding energy difference between the Si 2*p* peaks of the oxide layer and the silicon substrate plotted against the external voltage bias (red), where the difference with no bias is taken as the reference. The measured binding energy difference between the Au 4*f* peaks with and without 10 Mohm external resistance is also shown in the same graph (green). The measured binding energy difference between the Si 2*p* of the substrate and Au 4*f* does not change (blue). The experimental setup is also shown schematically. Using the curve of the Au 4*f* (with 10 Mohm), we can determine the magnitude of the two opposing currents due to: (i) Photoelectrons and secondary electrons going out of the sample, and (ii) stray electrons going into the sample.

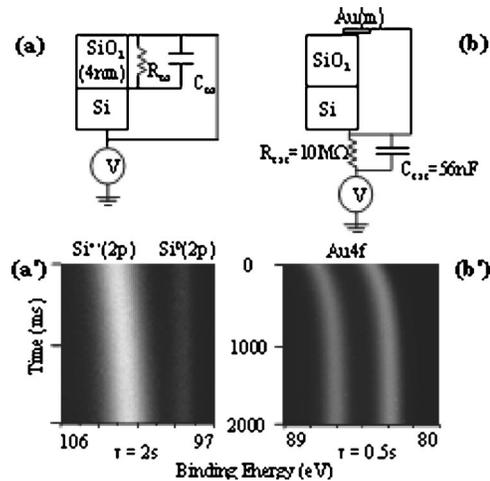


FIG. 3. 200 time-dependent XPS spectra of the Si 2*p* region for the SiO₂(4 nm)/Si system (a'), and the Au 4*f* region of a gold metal strip connected to an external 10 Mohm series resistor and a 56 nF parallel capacitor (b'). The schematics of the two systems are also shown in the upper parts [(a) and (b)]. First-order exponential fits give time constants of 2.0 and 0.50 s for the SiO₂/Si and the Au(m) with the external RC circuit, respectively.

Fig. 1. In this case, an additional potential (IR) develops as measured from the difference between the Au 4*f* levels with and without the external resistor which also exhibits an S type of a curve, also plotted in Fig. 2. With the help of these data, we can determine the magnitude of the various currents operative. The current due to the photoelectrons and secondary electrons is 18 nA (0.18 V/10 Mohm) as obtained from the plateau reached in the negative side of the curve since all low-energy stray electrons are repelled. Around +1 V applied potential, the null point is reached such that no difference can be measured between the Au 4*f* (as is) and Au 4*f* (10 Mohm) corresponding to cancellation of the currents going into and out of the sample. On the positive side, the plateau is not as clear but an approximate value of 42 nA can be obtained.

The more important point revealed by our measurements is the striking resemblance of the functional dependence of the curve of Au(m) with 10 Mohm external resistor to that of the SiO₂(4 nm)-Si(m) without the resistor (i.e., under these circumstances the SiO₂ layer behaves like a simple resistive element). Using this resemblance and the current values determined by Au and the external resistor, we can now derive an estimated resistance of 8.0 ± 1.0 Mohm to the 4 nm SiO₂ layer indicated as R_{ox} in the same figure.

As we have recently reported, it is also possible to pulse the voltage stress and obtain time-resolved data in the millisecond range.¹⁵ Figure 3(a) gives a set of 200 XPS spectra recorded with 10 ms steps of the Si 2*p* region of the same silicon sample containing the 4 nm oxide layer initially biased at -10 V but pulsed to +10 V to record the spectra. As can be seen from the figure, the Si⁰ peak is stable but the Si⁴⁺ peak shifts in time to lower binding energies. A first-order exponential decay fit gives a time constant of 2.0 ± 0.2 s. Following our strategy of establishing an equivalent circuit to the SiO₂/Si system, we have carried out a similar measurement on the gold metal connected externally through a resistance-capacitance (RC) circuit ($R=10$ Mohm, $C=56$ nF) as also shown in the Fig. 3(b) with perfect resemblance. The experimentally derived RC is 0.50 ± 0.5 s, which matches very closely the expected RC value of 0.56 s

10 Mohm \times 56 nF. With the help of these data, we can now assign an XPS-derived capacitance value of 250 ± 25 nF for the 4 nm SiO₂ layer using the XPS-derived resistance of ~ 8.0 Mohm and the time constant derived from the time-resolved measurement (2.0 s= 8.0 Mohm \times 250 nF). Hence, using simple voltage biasing in the dc and pulsing modes we turn the x-ray photoemission spectrometer into a noncontact tool for extracting electrical parameters of the surface structures.

We can compare the XPS-derived values to those obtained from the known geometry of the oxide layer (4 nm \times 4 mm \times 8 mm), resistivity and dielectric constant of the bulk silicon dioxide. Although we obtain a capacitance value of 250 nF using the dielectric constant of 3.6 for the silicon dioxide in perfect (but probably somewhat fortuitous) agreement with the XPS-derived value, we cannot obtain a reasonable value matching the XPS-derived resistance using the bulk resistivity of the silicon dioxide (10^{16} Ω m). A similar XPS-derived measurement was recently reported by Cohen as 0.83 Mohm/nm for the silicon oxide layer which is in the same order of magnitude but a factor of 2.4 smaller compared to our value.¹¹

We have also carried out measurements using oxide layers with different thicknesses and found again a more or less inverse correlation in capacitance but again no simple correlation exists for the resistance (for example, we derived values of 11 Mohm, and 36 nF for the resistance and the capacitance respectively, for a ~ 30 nm oxide sample). One should also keep in mind that the XPS-derived resistance values are related to trapping and detrapping of the holes created in the valence band of the oxide after the very fast (10^{-12} s) photoemission process and are derived under x-ray exposure.¹⁶ The time constants we measure are comparable to the time constants derived by time-dependent leakage currents determined for metal-oxide-semiconductor systems under x-ray exposure¹⁷⁻¹⁹ and/or using scanning capacitance microscopy.²⁰

Irrespective of the ways the XPS-derived electrical parameters relate to properties of the materials, we have demonstrated that XPS data, recorded under external dc together with pulsed voltage stimuli, can yield valuable information related to dielectric properties of the SiO₂/Si system. The approach is simple, versatile, and most importantly a non-contact measurement technique, which we expect to be most useful for investigation of fragile organic layers, where conventional electrical measurements are difficult.

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