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Differential Charging in X-ray Photoelectron Spectroscopy: A Nuisance or a Useful Tool?

Sefik Suzer*

Chemistry Department, Bilkent University, 06800 Ankara, Turkey

We apply a negative bias to the sample while recording an XPS spectrum to enhance differential (positive) charging. The enhanced differential charging is due to the repulsion of stray electrons from the sample, which normally cause partial neutralization of the poorly conducting samples or regions accumulating positive charging, as a consequence of the photoelectron emission. This enhanced differential charging (obtained by negative biasing) is shown to have the ability to separate otherwise overlapping peaks of PDMS layer from that of the SiO_2/Si substrate. Each layer experiences different charging that can be used to derive information related to dielectric properties of the layers, proximity of the atoms within composite multilayers, or both. Hence, differential charging in XPS, which is usually considered as a nuisance, is turned into a useful tool for extracting additional information from nanometer-size surface structures.

X-ray photoelectron spectroscopy (XPS), combined with various depth-profiling techniques, is a powerful tool for extracting chemical and structural information from surface structures in the nanometer scale. However, analysis of poorly conducting samples has always been problematic due to positive charging (commonly referred as surface charging or differential charging) as a result of incomplete neutralization of the photoemitted electrons.[1−6] Use of a low-energy electron flood gun, for neutralization, has been quite successful for most applications.[7,8] Overneutralization (using the flood gun) leading to excess negative charging is also frequently encountered.

Numerous publications have also appeared reporting constructive use of this surface charging (mostly negative) phenomenon for elucidating chemical or structural parameters of various materials. Lau and co-workers[9−15] have published several articles dealing with various structural or electrical properties of ultrathin dielectric films on semiconductors by utilizing the surface-charging. Thomas et al.[16] were able to separate the surface spectrum (mainly silicon dioxide) from the silicon substrate spectrum, (consisting of contamination and silicon dioxide on silicon), by use of surface charging; and similar applications were also reported by Ermolieff et al.[17] and Bell and Joubert,[18] while Miller et al. applied the technique to separate the XPS signals of the fiber from the exposed matrix at fractured surfaces.[19] Elegant use of surface charging for lateral differentiation of mesoscopic layers and for depth profiling in 1−10-nm thin layers have recently been reported.[20,21] In all of these studies, surface charging was controlled or varied via a low-energy electron flood gun resulting in mostly negatively charged surfaces, whereas, as we attempt to demonstrate in the present article, useful information can also be extracted by analysis of positively charged surfaces. We do not attempt to neutralize the charging developed and further achieve enhanced positive charging by application of a negative voltage bias to the sample while recording the XPS spectrum.

Application of external bias to the sample is not new and goes back (three decades) to the early days of XPS.[1,2] However, utilization of it for extracting chemical or structural information is scarce. One successful application was recently reported by Havercroft and Sherwood,[22] where it was demonstrated that biasing the sample holder with a large negative dc voltage (25−100 V) could be used to identify chemical differences in oxide films on an aluminum alloy. We have similarly reported that application of small (1−10 V) negative bias leads to enhanced differential charging by repelling the stray electrons within the vacuum system. The positive bias acts in the opposite way and

* E-mail address: suzer@fen.bilkent.edu.tr.

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reduces charging between the oxide layers and the underlying metal substrates.[23−25]

In this contribution, we demonstrate that application of a small negative bias on the sample holder during recording of XPS spectra can also lead to (i) separation of otherwise unresolved spectral features or (ii) extraction of useful dielectric and proximity information about nanometer-scale surface structures.

EXPERIMENTAL SECTION

Oxide layers were grown thermally on HF-cleaned Si (100) substrates at 500 °C in air. Poly(dimethylsiloxane) (PDMS), having an average molecular weight of 10 000, was obtained from Goldschmidt AG (Essen, Germany) and was dip-coated onto the SiO_2/Si substrates from its dilute THF solution. Citrate-capped gold nanoclusters were prepared according to the well-established procedure and were directly deposited from their aqueous solutions onto the SiO_2/Si substrates.[26,27] In a different experiment, citrate-capped gold nanoclusters were first mixed with 1.0 g of tetraethoxysilane (TEOS; Aldrich). The resulting solution was then acidified with 1.0 mL of 0.01 M HNO_3 solution and was coated onto the SiO_2/Si substrate to affect partial hydrolysis and polymerization of TEOS by evaporation of water and ethanol.

A Kratos ES300 electron spectrometer with Mg Kα X-rays (nonmonochromatic) is used for XPS analysis. A typical sample is a ~1-mm-thick silicon wafer with dimensions of 4 × 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 takeoff 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.

RESULTS AND DISCUSSIONS

(a) Resolution of Overlapping Features. Figure 1 depicts the Si 2p region of the sample containing a very thin layer of PDMS on the SiO_2/Si substrate. When the sample is grounded, only two peaks appear (Figure 1a). The peak at lower binding energy can be assigned to the silicon metal underlayer at 99.7 eV, whereas, the broad feature centered around 103.8 eV is a composite and overlapping peaks of silicon atoms of both the PDMS and the oxide layers. The tabulated values of bulk PDMS and SiO_2 are 102.4 and 103.4 eV, respectively, and are lower than the measured one because the charging is already operative.[8,23] Upon application of a negative bias (Figure 1b and c), the metal peak moves to higher binding energy (lower kinetic energy), and the composite peak gets separated into an oxide peak, which also moves with the bias, whereas the second one stays unaffected, which can now be assigned to PDMS. As will be elaborated in the next section, the origin of these shifts is related to charging capacity of the layers due to photoemission and their partial

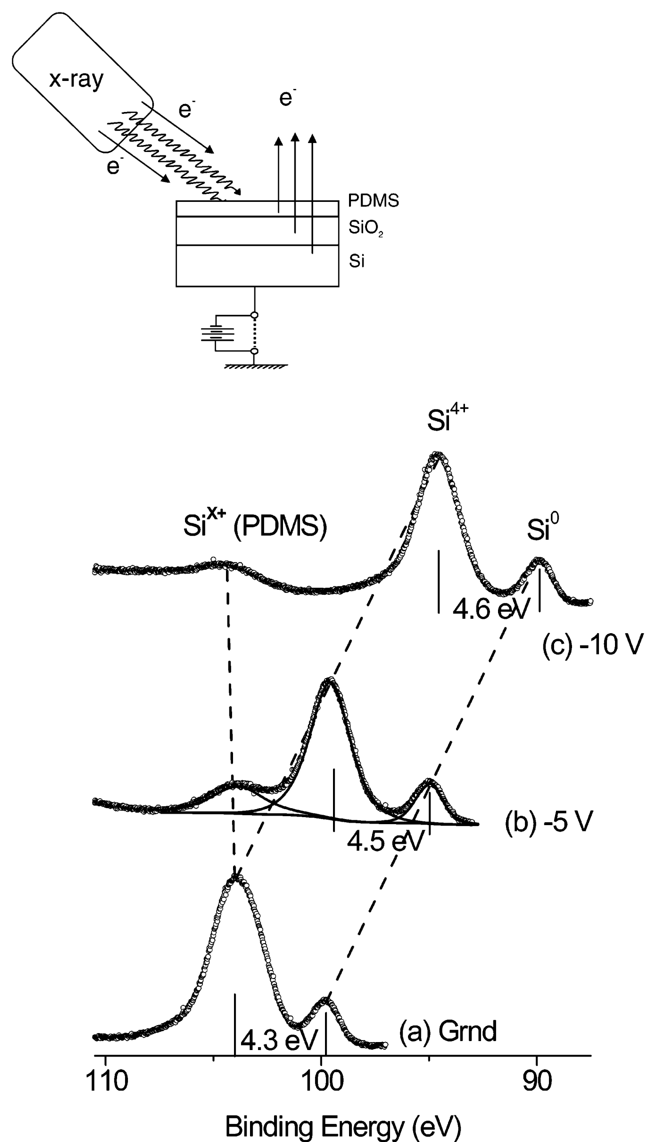

Figure 1. XPS spectra of the Si 2p region of PDMS deposited (by dip-coating) onto a silicon substrate containing a ~6-nm oxide layer recorded at 90° takeoff angle. The sample is (a) grounded or (b) biased with −5 or (c) −10 V. A schematic diagram of the experimental setup is also included on top. The electrons originating from the X-ray tube represent the low-energy stray electrons.

neutralization by the stray electrons falling onto the sample. When the sample is grounded, which is the most common practice, a fraction of low-energy stray electrons within the vacuum system falls onto the sample and causes partial neutralization. When biased positively, a larger fraction of stray electrons is collected by the sample causing more neutralization. However, when the sample is under negative bias, stray electrons are repelled with the consequence of even more charging. As also depicted in Figure 1, the most likely origin of the stray electrons is the X-ray tube.

This added resolution is also manifested both in the O 1s and the C 1s (not shown) peaks as depicted in Figure 2, where the regions are recorded at 60° and 30° electron takeoff angles. The purpose of this figure is 2-fold: (i) to emphasize that the shifts associated with differential charging apply to all peaks (and all regions), and (ii) to use the angle-resolved data for deriving

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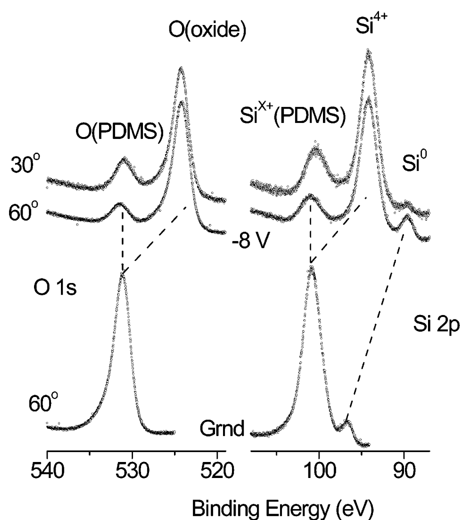

Figure 2. O 1s and Si 2p regions of the same sample (as in Figure 1) recorded grounded and under −8 V at 60° and 30° electron takeoff angles (to enhance surface sensitivity).

stoichiometric and depth information about these nanometer layers.[28] Accordingly, the thickness of the oxide layer and the PDMS layer are estimated as 6 and 1 nm, respectively, assuming a uniform distribution. The derived atomic composition for the PDMS ($C_{1.0}Si_{0.40}O_{0.45}$) is also not drastically different from the theoretical composition ($C_{1.0}Si_{0.50}O_{0.50}$).

(b) Dielectric Properties. Another important observation is the apparent increase in the measured binding energy difference between the oxide and the metal peaks. As also indicated in Figure 1, this difference is 4.3 eV when the sample is grounded and increases to 4.5 and 4.6 eV when it is biased with −5 and −10 V, respectively. In other words, when the measured binding energy is plotted against the applied negative bias, the Si 2p peaks of the metal and the oxide have slopes of 0.99 and 0.86, respectively; whereas the binding energy of the PDMS peak does not change at all (i.e., the slope is ~0). As was also mentioned above, by applying a negative bias, stray electrons within the vacuum chamber, which normally cause partial neutralization of the charging, are now repelled and induce additional charging, and each layer is influenced differently.

One oversimplified approach is to relate the potential developed in a layer, as a result of charging, with the capacitance of the layer, assuming that they behave lik parallel-plate capacitors:

$$\Delta V_L^C = Q_L/C_L = Q_L(d_L/\epsilon_L)$$

where Q_L is the charge accumulated on the layer, d_L is the thickness, and ϵ_L is the dielectric constant.[25] Although it is difficult to estimate the charge accumulated in each layer, the general strong inverse dependence on the dielectric constant is noteworthy. In light of our experimental findings, we can now postulate that the PDMS, an organosilicon layer, having a low dielectric constant ($\epsilon \approx 2.5$) experiences a more severe charging compared with the silicon oxide layer with ($\epsilon \approx 4.4$) which in turn charges more than the silicon metal underlayer. The fact that the Si 2p

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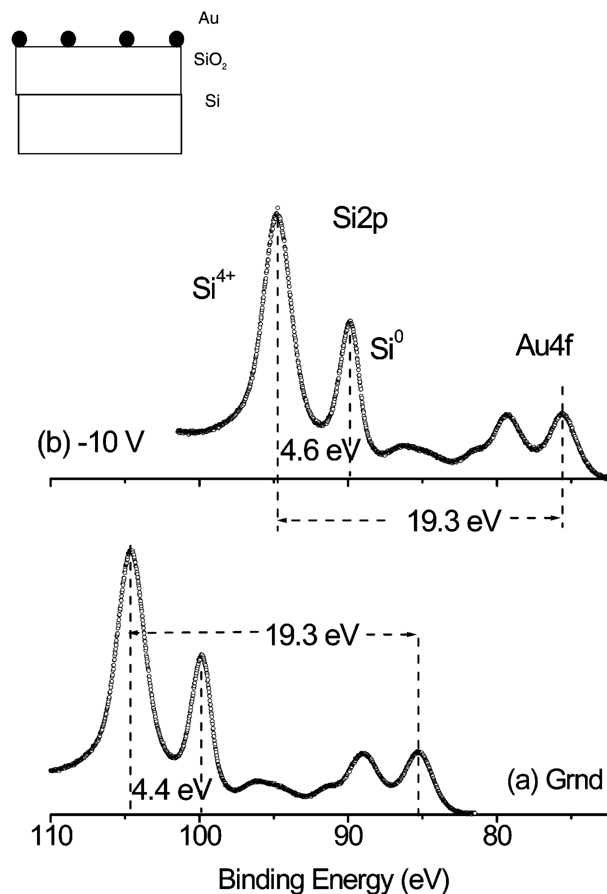

Figure 3. Si 2p and Au 4f regions of a similar substrate containing gold nanoclusters deposited directly on the oxide layer and recorded when the sample is (a) grounded and (b) under −10 V bias.

peak belonging to the PDMS layer becomes broader with voltage bias (Figure 1c) is more evidence of the severe charging of this layer. However, other chemical and structural factors, influencing charging and discharging mechanisms, need to be considered in detail in order to correlate the charging behavior with certain dielectric properties of these structures. Alternatively, as we advocate in the present study, the XPS-derived data, via application of dc or ac bias, can be utilized to extract such information.

(c) Proximity Information. In our previous study, we demonstrated that nanoclusters of gold deposited directly on the SiO_2/Si substrate move with exactly the same magnitude and direction as the oxide layer under external bias.[23,24] This was attributed to the fact that the gold nanoclusters experience differential charging similar to that of the oxide layer rather than the silicon underlayer, which is also reproduced in Figure 3. As is evident from the figure, although the binding energy difference between the Si 2p peaks of the oxide and the silicon increases (from 4.4 to 4.6 eV) with the bias, the difference between the Si 2p peak of the oxide and the Au 4f peak stays constant at 19.3 eV.

When the gold nanoclusters are embedded into another thin polymer layer (TEOS in this case), they experience the same differential charging as their host (TEOS) as shown in Figure 4. Here again, the silicon 2p of the TEOS layer overlaps with that of the oxide when the sample is grounded but gets separated after application of a negative bias since the oxide peak moves with the bias. The Au 4f peaks stay unshifted like the Si 2p of the TEOS,

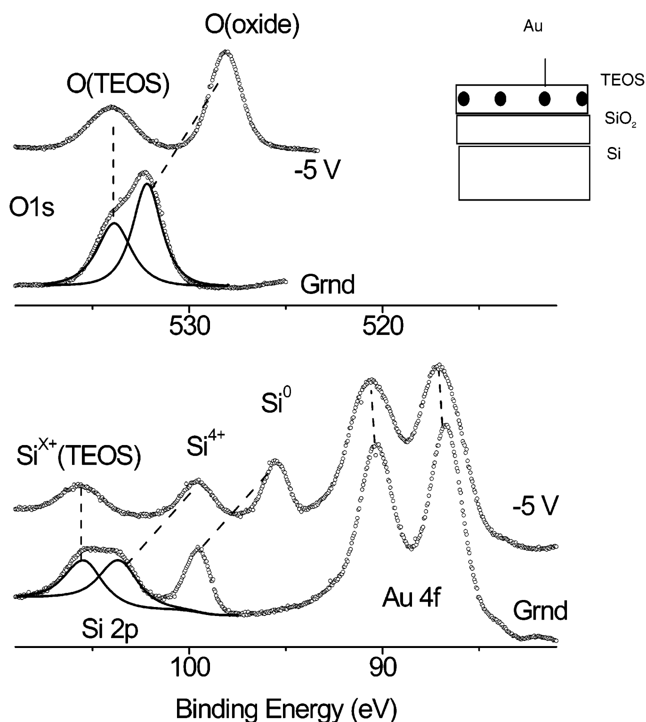

Figure 4. Si 2p−Au 4f and O 1s regions of a similar substrate and TEOS layer containing embedded gold nanoclusters recorded when the sample is grounded and under −5 V bias.

and both the O 1s and the C 1s (not shown) peaks are split into two components, one of which can be assigned to the TEOS and the other to the substrate, solely on the basis of their behavior under bias.

The chemical composition of the TEOS layer determined from the XPS data ($C_{1.0}Si_{0.30}O_{0.50}$) is similar to that of PDMS, indicating also similar charging/dielectric behavior. Hence, the gold nanoclusters, in this case, experience similar charging as their host (TEOS) and not as the substrate. In addition to the added resolution offered by biasing, the proximity of the gold nanoclusters to the Si atoms in the TEOS layer (since they move together under bias) can easily be deduced without prior knowledge of their preparation scheme.

CONCLUSIONS

Enhanced negative differential charging, which can be accomplished by simple biasing of the sample, not only can lead to separation of overlapping peaks but it can also give important dielectric and proximity information in composite multilayers. XPS analysis under an external bias opens new avenues for extracting useful and noncontact structural and dielectric properties of nanometer-size structures.

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