Methods for probing charging properties of polymeric materials using XPS

Hikmet Sezen, Gulay Ertas, Sefik Suzer*

Department of Chemistry, and Institute of Materials Science and Nanotechnology, Bilkent University, 06800 Ankara, Turkey

ARTICLE INFO

Article history:

Available online 17 April 2009

Keywords:

Charging
Polymeric materials
Dynamics of charging
Resistance
Capacitance
Dielectric properties

ABSTRACT

Various thin polystyrene, PS, and poly(methyl methacrylate), PMMA and PS + PMMA blend films have been examined using the technique of recording X-ray photoelectron spectrum while the sample is subjected to ± 10 V d.c. bias, and three different forms of (square-wave (SQW), sinusoidal (SIN) and triangular (TRG)), a.c. pulses. All films exhibit charging shifts as observed in the position of the corresponding C1s peak under d.c. bias. The a.c. pulses convert the single C1s peak to twinned peaks in the case of the square-wave form, and distort severely in the cases of the SIN, and TRG forms, and all three of them exhibit strong frequency dependence. In order to mimic and better understand the behavior of these polymeric materials, an artificial dielectric system consisting of a clean Si-wafer coupled to an external 1 M Ω resistor and 56 nF capacitor is created, and its response to different forms of voltage stimuli, is examined in detail. A simple electrical circuit model is also developed treating the system as consisting of a parallel resistor and a series capacitor. With the help of the model, the response of the artificial system is successfully calculated as judged by comparison with the experimental data. Using one high frequency SQW measurements, the off-set in the charging shift due to the extra low-energy neutralizing electrons is estimated. After correcting the corresponding off-set shifts, the XPS spectra of the three different PS films, one PMMA, and one PS + PMMA blend film are re-examined. As a result of these detailed analysis, there emerges a clear relationship between the thicknesses of the PS films with their charging abilities. In the blend film, PS and PMMA domains are electrically separated, and exhibit different charging shifts, however, the presence of one is felt by the other. Hence, the PS component shifts are larger in the blend, due to the presence of PMMA domains, which has intrinsically a larger R_{eff} , and conversely the PMMA component shifts are smaller due to the presence of PS domains.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Although it has been more than 5 decades since its first introduction, X-ray photoelectron spectroscopy (XPS) still keeps its pivotal position among the various surface analytical techniques, due to its ability in resolving chemical identity of atoms, from measured binding energies via the photoemission process [1]. During data acquisition in XPS, a finite, measurable, and more or less steady current (0.1–20 nA) flows through the sample, due to the generated photo and secondary electrons, which usually causes unwanted positive charging in poorly conducting samples or parts of surface heterostructures [2–5]. A great deal of effort has been devoted to compensate and overcome this charging, and very successful techniques have been developed, mostly using directed flow of low energy electrons (or ions) from an external unit (flood-gun) to the sample [1]. Excessive flooding can also cause negative charging [6–8]. This negative charging, dubbed as controlled surface charging (CSC), has also been

utilized in extracting additional chemical/physical properties of surface structures, even down to monolayers [3–10]. For example, it was shown that monolayer films are not affected, but multilayer films are affected by the voltage applied [9,10]. Islam and Mukherjee have used the positive charging to derive information about the structure of Langmuir–Blodgett films of cadmium arachidate on silicon substrate [11]. A recent elegant application reported by Cohen and co-workers has extended the technique to profile the submolecular potentials developed across organic monolayers [12].

However, in majority of applications, the emphasis in XPS, until now, has mostly concentrated on recording of the line positions (and intensities) and/or fine structures like spin-orbit splitting, shake-up satellite structure, etc. Except in few cases, and in Cohen's recent efforts [13–20], incorporation of electrical measurements for extracting additional information has not been extensive.

During an XPS measurement, the total current flowing through a sample is the sum of electrons, going out of the sample; due to photoemission, and almost as importantly, secondary electrons [21,22], and into the sample; due to electrons or ions from the flood-gun(s) or stray electrons. Some components of the total current can easily be controlled by application of a small (0–10 V)

* Corresponding author. Tel.: +90 312 2901476; fax: +90 312 2664068.
E-mail address: suzer@fen.bilkent.edu.tr (S. Suzer).

external voltage bias, both in the form of d.c. and/or a.c. pulses, as it has been reported recently [17–30]. The effect of this applied voltage-bias can then be assessed in the measured line positions. If the sample under investigation is a good conductor, the effect will manifest itself as trivial voltage shifts in the positions, equivalent to the applied bias. For poorly conducting samples, however, this will emerge as non-linear shifts due to operation of various charging/discharging processes, which can be utilized for extracting both static and dynamic information about these processes, when, respectively, d.c. and a.c. bias are applied. 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 [31–34]. Photoemission, utilizing UV, X-rays and lasers, has also been employed for probing very fast ($<10^{-9}$ s) charging dynamics [35–37]. Core-level X-ray photoemission, XPS, is especially attractive since additional chemical information can be derived from the line positions of the corresponding peaks, since the measured line-positions are altered by local potentials developed, due to the uncompensated charges.

In this work, we will review our recent work on applications to some polymeric materials, of voltage bias in d.c. and pulsed forms using square-wave (SQW), sinusoidal (SIN), and triangular (TRG) excitation with varying frequencies, and present the corresponding XPS spectra as response. Organic dielectric materials (mostly in polymeric nature) are important class of materials utilized for various applications, and charge accumulation/dissipation is pivotal for their advanced functionalities [38–40].

Previously reported dynamical photoemission measurements have been either in the ultra-fast, sub-pico seconds regime using laser excitations [35–37], or in a much longer time regimes (10^1 to 10^4 min) with conventional XPS measurements [5,41–45]. Our measurements fill this gap and provide information about charging/discharging dynamics of dielectric materials in the range of 10^{-3} to 10^3 s, matching those of many important chemical–biochemical processes [46].

2. Experimental

A Kratos ES300 electron spectrometer with MgK α X-rays (non-monochromatic) is used for XPS measurements, and a near-by filament provides low energy electrons for charge neutralization. The polymers used in this work are polystyrene, PS, and poly(methyl methacrylate), PMMA, purchased from Aldrich. Polymer solutions, prepared by dissolving in chlorobenzene, are used for making films by spin-casting onto Si(100) substrates. 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. For probing charging or electrical properties, the samples are subjected either to ± 5 V (in some cases ± 10 V) d.c. stress or to various a.c. pulses like SQW, TRG, and SIN, of different amplitudes and with varying frequencies in the 10^{-3} to 10^3 Hz range, while recording XPS data. An artificial dielectric system, created by connecting an external series resistor and a parallel capacitor to a clean p-Si wafer was also investigated for comparison purposes. We have also developed a simple model, treating a homogeneous surface layer as consisting of a series resistor (R) and a parallel capacitor (C), for calculating/simulating the dynamic behavior of surface structures. For comparison, we have also reproduced some of the previously published data on films of PS, PMMA and a blend of them (PS + PMMA), where the XPS data were recorded at eight different frequencies for all three samples [26]. We refer to this procedure as the full frequency analysis.

3. Results and discussions

3.1. Charging of thin PS films under d.c. bias

Charging shifts are encountered more frequently in XPS analysis of polymeric materials, and one of the experimental tricks for minimizing such effects is to spin-coat a very thin film of these polymers on conducting and flat substrates, for which reasonably conducting silicon wafers are commonly employed [48]. In Fig. 1, we display the C1s spectrum of very thin three polystyrene films, with different thicknesses, spin-coated on a silicon substrate, recorded while the samples are grounded and also when +10 and -10 V d.c. bias applied. As can be gathered from the figure, the positions of the C1s peak in the grounded case for all three samples are different from the reference value of 284.8 eV [49]. Similarly, the positions of all the biased peaks are also different from their expected values with respect to the applied bias. Normally, for a conducting sample, application of -10 V bias would result in a +10.0 eV shift to higher kinetic energy (blue-shift) since electrons gain extra energy due to the applied potential, which simply manifest itself as -10.0 eV shift in the binding energy scale, and correspondingly the +10 V bias would cause a red shift. However, the observed shifts under -10 V bias are around -8.5 to -9.0 eV, for all the three samples, which means that a +1.5–+1.0 V differential charging shifts develop with respect to their grounded samples. Note also that the three grounded samples are also charged. The shifts under +10 V are even more dramatic and exhibit strong thickness dependence. All these charging shifts arise, in addition to some dielectric property of the material under consideration, from a combination of the variations in the currents due either to the electrons generated from the sample or the electrons falling on to the sample, which are affected nonlinearly by the applied bias.

Using a simple minded approach we can try and relate the observed charging shifts to the $(IR)_{\text{drop}}$ arising from the various currents, falling on to the sample and passing through it, and by assigning an effective resistance (R_{eff}) to the sample under investigation [50]. Similarly, the response of the system to the time-varying (a.c.) biases may also be accounted for if we were to assign an effective capacitance (C_{eff}) to the sample. Implicit in this approach is that one can represent the dielectric property of polymeric materials by assigning an effective resistance (R_{eff}) and capacitance (C_{eff}), respectively, and relate them to some measurable

Fig. 1. C1s region of the XP spectra of three different PS films spin-coated on a silicon wafer are shown, recorded when the sample is grounded (olive) and under +10 (red) and -10 V (blue) external bias. The inset on the top left depicts the experimental set-up, where FG stands for the function generator. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Fig. 2. (a) The variation of the current passing through the sample under various bias conditions; (b) calculated $(IR)_{\text{drop}}$ using the current values at +5 and –5 V, respectively; (c) XP spectrum of the Si2p region of a clean Si wafer, recorded when grounded; (d) the Si2p region of the artificial dielectric system of Si(m) + RC, under +5 V and –5 V external d.c. bias.

quantities like the thickness of the film and more importantly to the chemical nature and composition. But the challenge is to entangle the charging shifts arising from the extra low energy electrons provided by the flood-gun or the neutralizing source(s), which is the main theme of the present contribution, as will be presented below.

Before we attempt to analyze the response of the polymeric dielectric systems, we will first introduce an artificial dielectric system, created by incorporating an external circuit comprising of a series resistor, R_{ext} , and a parallel capacitor, C_{ext} , to a highly conducting sample to test the methodology.

3.2. The artificial dielectric: Si(m) + $R_{\text{ext}}C_{\text{ext}}$

As mentioned above, the simplest system for relating the experimentally measured charging shifts in the binding energies (BE) to the charging/discharging state, capacity, and/or electrical property of the dielectric material under consideration, can be created by connecting a conducting silicon sample to a series $1\text{ M}\Omega$ resistor (R_{ext}) and a 56 nF parallel capacitor (C_{ext}), since the Si2p XPS peak recorded when grounded is relatively narrow, as shown in Fig. 2(c), to allow us follow the shifts as well as broadenings of the representative peak(s). In Fig. 2(a), we show the measured electron current passing through the sample, which consists of three major components; (i) photoelectrons and secondary electrons generated, (ii) stray electrons within the vacuum system, stemming from ion-gauges, etc., (iii) low energy electrons from the filament. Except for the photoelectron current, the others are strongly affected by the applied bias. Fig. 2(d) depicts the Si2p spectra recorded when the system is d.c. biased to +5 V (red) and –5 V (blue), respectively. Whereas, the Si2p peak faithfully shifts –5.0 eV under –5 V bias, it

Fig. 3. (a) Schematic representation of triangular, square-wave and sine-wave excitations; (b) XP spectrum of the Si2p region of a clean Si wafer, recorded when grounded; (c) the Si2p region of the artificial dielectric system of Si(m) + RC, when subjected to three different excitations (SQW, SIN, TRG) at 1.0 and 40 Hz, respectively.

only shifts +2.1 eV under +5 V bias, which is simply related to the expected $(IR)_{\text{drop}}$ arising from the $2.9\text{ }\mu\text{A}$ current passing through the sample (and the $1\text{ M}\Omega$ external resistor), schematically shown as the red bar in Fig. 2(b). Note also that under –5 V bias, only the small current of ca. 10 nA, stemming from the photoelectrons, going out of the sample, is operative to yield only an insignificant ($10\text{ nA} \times 1\text{ M}\Omega = 0.010\text{ eV}$) shift, schematically shown as the blue bar in Fig. 2(b). It is also determined through measurements that under progressively more positive potentials the shifts follow faithfully the $(IR)_{\text{drop}}$ predicted by the measured current at each potential. This finding naively gives us the hope to relate the measured shifts to an effective resistance of the sample or surface structures under investigation, once we know the (effective) electron current.

The presence of a capacitor, whether within the sample or purposely incorporated externally, can only be detected when the sample is subjected to a time-varying stimuli in the form of triangular, square-wave, or sinusoidal excitations as shown in Fig. 3, for the case of the artificial dielectric system of Si(m) + $R_{\text{ext}}C_{\text{ext}}$, and in Fig. 4 for one of the PS films. It is clear from both figures that all three excitation exhibit strong frequency dependence which can be related to an effective capacitance. The simple grounded spectrum

Fig. 4. The C1s region of the 20 nm PS film when subjected to three different excitations (SQW, SIN, TRG) at 0.001 and 40 Hz, respectively.

Fig. 5. (a) XP spectrum of the Si2p region of the artificial dielectric system of Si(m) + RC, under +5 and –5 V external d.c. bias; (b) XP spectrum of the Si2p region of a clean Si wafer, recorded when subjected to 0.4 and 40 Hz SQW excitation; (c) clean Si + R only at 40 Hz; (d) Si(m) + RC at 0.4 Hz; (e) Si(m) + RC at 40 Hz.

of a single Si2p (and C1s) peak gets complicated, yielding at best twinned peaks for the SQW-wave-excitation, but distorted shapes for the SIN and TRG excitations. The similarity among the three excitations is that in each case, and in the low frequency spectra, the features (the twinned peaks in the SQW case, etc.) are closer to each other, indicative of larger charging shifts.

Since, the case of the SQW-excitation is the simplest, at least in visual resemblance to the original spectrum, in the present contribution, we will only present its application and analysis. In Fig. 5, we display the spectra obtained by application of the square-wave excitation under various conditions to our artificial dielectric system, the Si(m) + RC. In Fig. 5(a), the spectra recorded +5 and –5 V d.c. are given which were also displayed in Fig. 2(d), and reproduced only for comparison purposes. Fig. 5(b) shows the SQW application at 0.4 and 40 Hz to the sample without R nor C, twinning the Si2p peak, respectively, at –5.0 and +5.0 eV positions, i.e. no charging shift is operative at all. Fig. 5(c) shows the 40 Hz application to Si(m) + R only, which is equal to the case of two different d.c. applications separately, shifted by the $(IR)_{\text{drop}}$ at each point, which is also equal to the low frequency application at 0.4 Hz, displayed in Fig. 5(d), since ample time is allowed, the capacitor is caught in its fully charged or discharged state. At the higher frequency of 40 Hz, shown in Fig. 5(e), the full 10.0 eV difference is resumed but the positions of the peaks are off-set by 1.8 eV, due to the average current $(I_{\text{avg}}R)_{\text{drop}}$ passing through the circuit, which will be elaborated more in the next section. As we will discuss below, the presence (or absence) of this off-set can be very useful in relating with charging capacity and/or state of the dielectric under investigation.

Fig. 6. The circuit used for simulations.

3.3. The model

A simple circuit model of a dielectric film having a resistance R, and a capacitance C can be constructed as shown in Fig. 6, where the electron gun and the photoelectron currents are modeled by a voltage controlled current source (VCCS). The nonlinear voltage–current curve for the VCCS is extracted through analysis of a series of XPS measurements by applying d.c. voltages to the silicon sample in series with a known external resistor, which was already depicted in Fig. 2(a). The VCCS current–voltage dependence is assumed to be the same for all the samples, and throughout the entire dynamic measurements. The excitation voltage source $V_{\text{EX}}(t)$, which is supplied externally by the function generator, can be a time varying voltage with any shape (TRG, SQW, SIN, etc.). In order to calculate the XPS spectra, we need to solve the differential equation describing the change of the surface potential $V_s(t)$ given by

$$C \frac{d(V_s - V_{\text{EX}})}{dt} + \frac{V_s - V_{\text{EX}}}{R} + I_s(V_s) = 0 \quad (1)$$

where R and C are, respectively, the effective resistance and the capacitance between the surface and the source as shown in Fig. 6, and $I_s(V_s)$ is the surface potential dependent current, mentioned above and given in Fig. 2(a). Therefore, solutions can be obtained numerically for any arbitrary excitations $V_{\text{EX}}(t)$, like SIN, SQW, TRG, etc.

By solving numerically the Eq. (1) for the values of $R = 1.0 \text{ M}\Omega$ and $C = 56 \text{ nF}$ for the SQW excitation, we calculated the time variation of the shifts of the peaks at certain time increments, which are shown in Fig. 7(a) for three different frequencies. It can be seen that, depending only on the frequency of the excitation and charge-discharge time constants (product of resistance and capacitance values) of the system, the left and right peaks shift differently. The simulated XPS spectrum $S_{\text{XPS}}(v)$ can now be calculated by shifting the original spectrum S_0 obtained by grounding the sample as much as calculated shift of the surface potential of the sample at each time increment as was shown in Fig. 7(a) for three different frequencies. The resultant calculated spectrum at each frequency is obtained by summing the spectra at each increment and dividing the resultant spectrum by the number of time increments used. The calculated spectra, as well as the measured ones are displayed in Fig. 7(c), where the agreement between the two sets is remarkable.

At the low frequency applied (0.4 Hz), the capacitance is bypassed since the system charges or discharges very quickly and the data resembles that of the d.c. cases where the difference between the peaks is 7.1 eV. At the moderate frequency of 4 Hz, the peaks are broadened somewhat, and the difference between the peaks gets larger, 8.5 eV (approaching 10 eV). At the higher frequency of 40 Hz, the 10.0 eV difference between the peaks is resumed, except again the centre is 1.8 eV off-set from the ground position, which can be used to measure the $(I_{\text{avg}}R)_{\text{drop}}$ for enabling us to assess the charging state and/or the capacity of the sample under investigation. Note also that both the positions of the twinned peaks,

Fig. 7. (a) Simulated SQW excitation at three different frequencies; (b) XP spectrum of the Si2p region of a clean Si wafer, recorded when grounded; (c) the simulated and measured Si2p region of the artificial dielectric system of Si(m) + RC at three different frequencies.

as well as their broadenings are faithfully reproduced through our calculation. Hence, with the help of the model, there seems to be a real hope that important information can be derived about the sample under investigation using the frequency data. For example, let us take the data at the high frequency of 40 Hz. Knowing that the charge is accumulated in the external RC circuit, we would not expect any permanent charge accumulation on the Si(m) sample. As a result, the positions of the positive and the negative peaks are equally shifted by the average current passing through the system. This average current can be estimated to be approximately half of the current measured under +5 V bias, since the current under −5 V is practically zero, and the system alternates and spends 50% of its time at these two polarities several times during data gathering. Accordingly, we would expect $I_{\text{avg}} = 2.90/2 = 1.45 \mu\text{A}$ to cause an average shift of 1.45 eV for the center of the peaks from that of the grounded Si2p peak. The measured shift of 1.8 eV indicates that the actual a.c. current at 40 Hz is somewhat larger. Whatever their values are, the measured off-sets at the high frequency limit can be safely used to estimate the variations in the effective resistance (R_{eff}) of the sample under investigation, assuming the average currents do not change significantly from one measurement to the other, as we will demonstrate by application to the three different PS films mentioned in Section 3.1.

3.4. The charging shifts and thickness of the PS films

Fig. 8 displays the C1s XP spectra of the 20, 35 and 55 nm PS films, recorded when they are subjected to 40 Hz SQW excitation with $\pm 10\text{V}$ amplitude. In all three cases, the C1s peak is twinned with exactly 20.0 eV separation, however the spectra are off-set in energy. Moreover, this off-set increases with the thickness of the film, which is a celebrated result. Assuming the I_{avg} to be the same for all of the three samples, we can now attribute this increase to the increase in the effective resistance, R_{eff} , with an increase in the thickness of the film, although the 0.6 eV difference between the 35 and 20 nm samples ($\Delta d = 15 \text{ nm}$), and the 2.2 eV difference between the 55 and 35 nm samples ($\Delta d = 20 \text{ nm}$) corresponds to a somewhat stronger than a linear dependence.

Another way of utilizing these measured off-set differences at the high frequency end of the three samples is to go back and rean-

alyze the d.c. shifts displayed in Fig. 1, as shown in Fig. 9, where the peaks of the 35 and 55 nm films are shifted back by 0.6 and 2.2 eV, respectively, corresponding to the difference of the off-set shifts from that of 20 nm film. Looking first to the C1s peaks recorded when the films are grounded, shown in the center, we can now realize that the thicker films are caught in progressively more and more positively charged states (positive slope). Under −10 V bias, the charging is even more severe (a larger positive slope). But under +10 V bias all films are negatively charged (negative slope). The erratic shifts shown in Fig. 1 are normalized and assigning an effective resistance, R_{eff} , increasing with the thickness of the PS film is justified.

3.5. The charging shifts in PS + PMMA blends

As was reported in one of our previous studies, charging behavior of thin PS and PMMA films are widely different from each other and a blend film of the two has a behavior in between the two, with also a clear indication of phase separated PS and PMMA domains [26]. Similarly, and after correcting for the off-set shifts determined

Fig. 8. The C1s region of the three different PS films when subjected to the SQW excitation at 40 Hz, respectively.

Fig. 9. The C1s spectra of the three different PS films shown in Fig. 1, after correcting for the off-set due to the $I_{\text{avg}}R_{\text{drop}}$ (see the text).

from the high frequency SQW spectra, the C1s regions for the 20 nm PS and ca. 15 nm PS + PMMA films are displayed in Fig. 10 under various d.c. bias conditions. The C1s spectra of the blend film are fitted to 1 C–H component belonging to PS, and three components of the PMMA (C–H, C–O, and C=O) using the tabulated energy differences, and also the intensity ratios between them [49]. From the figure one notices immediately that the charging shifts of the PS components in the blend film are larger than those of the pure PS film, and conversely, the charging shifts of the PMMA components are smaller than those of the pure PMMA film (not shown), which are 7.0 eV between the ground and –10 V, and 5.6 between the ground and +10 V. Hence, although each component shifts separately, and more or less independently within the blend film, the presence of one is felt by the other through the charging shifts measured. Hence, the PS component charging shifts are larger due to the presence of PMMA domains which has a larger R_{eff} , and conversely the PMMA component shifts are smaller due to the presence of PS domains.

The full frequency analysis of the PS, PMMA and PS + PMMA blend films, which was reported in our earlier study, which is also reproduced in Fig. 11 for comparison, is quite a lengthy procedure. This procedure involves recording the binding energy difference between the twinned peaks at several frequencies (8 in the case of the data presented in Fig. 11), covering the full range of 10^{-3} to 10^3 Hz [26]. As we have tried to show in the present study, that

Fig. 10. The C1s spectra of the 20 nm PS, and the 15 nm blend film of the two polymers (PS + PMMA), after correcting for the off-set due to the $I_{\text{avg}}R_{\text{drop}}$ (see the text).

Fig. 11. Complete frequency dependence of the measured binding energy difference between the twinned peaks under SQW excitation of the 20 nm PS, PMMA and together with a 15 nm blend film of the two polymers (PS + PMMA). This was also given in Ref. [26].

almost the same qualitative information can be extracted using the d.c. shifts, and, more importantly, using only one high frequency SQW excited spectrum, together with the help of the model. The latter procedure corresponds to approximately 1/10 factor of reduction in data gathering time, when compared to the full frequency analysis one.

4. Conclusions

When applied to nonconducting dielectric samples, our method can extract an effective resistance (R_{eff}) and an effective capacitance (C_{eff}) of the films under X-rays and low energy electrons exposure, and the application of SQW excitation at the high frequency limit enables us to entangle the true charging shifts from those due to the extra low-energy electrons. The charging and discharging of the films are non-linearly dependent on the surface electrical field created since they are described by tunneling or hopping processes, but a clear dependence on the thickness emerges, which can be related to various material specific dielectric properties, like effective resistance and capacitance, dielectric breakdown behavior, etc.

The simple RC model can be replaced by a more accurate model that takes into account of the distribution of charge-traps. However, the ultimate model has to include E-field and position dependent charge-discharge rates as well as local density of trap states. Although we have presented, in detail, applications of only the SQW excitation, it is obvious that the SIN and TRG excitations would also yield similar information, especially when analogy between electrochemical properties like double-layer charging are sought for [46,51].

Acknowledgements

This work was partially supported by TUBA (Turkish Academy of Sciences) and TUBITAK (The Scientific and Technological Research Council of Turkey) through the Grants No. 106T409.

References

- [1] D. Briggs, M.P. Seah, Practical Surface Analysis, vol. 1, 2nd edition, Wiley, Chichester, 1996.
- [2] T.L. Barr, J. Vac. Sci. Technol. A 7 (1989) 1677–1683.
- [3] W.M. Lau, J. Appl. Phys. 65 (1989) 2047–2052.
- [4] W.M. Lau, X.W. Wu, Surf. Sci. 245 (1991) 345–352.

- [5] B.J. Tielsch, J.E. Fulgum, *Surf. Interface Anal.* 24 (1996) 422–427, 24 (1996) 459–468 and 25 (1997) 904–912.
- [6] I. Doron-Mor, A. Hatzor, A. Vaskevich, T. van der Boom-Moav, A. Shanzer, I. Rubinstein, S.R. Cohen, H. Cohen, *Nature (London)* 406 (2000) 382–385.
- [7] K. Shabtai, I. Rubinstein, S.R. Cohen, H. Cohen, *J. Am. Chem. Soc.* 122 (2000) 4959–4962.
- [8] A. Rozenblat, Y. Rosenwaks, L. Segev, H. Cohen, *Appl. Phys. Lett.* 94 (2009), Article No.: 053116.
- [9] M. Dubey, I. Gouzman, S.L. Bernasek, J. Schwartz, *Langmuir* 22 (2006) 4649–4653.
- [10] I. Gouzman, M. Dubey, M.D. Carolus, J. Schwartz, S.L. Bernasek, *Surf. Sci.* 600 (2006) 773–781.
- [11] A. Islam, M. Mukherjee, *J. Phys. Chem. B* 112 (2008) 8523–8529.
- [12] N. Filip-Granit, M.A. van der Broom, R. Yerushalmi, A. Scherz, H. Cohen, *Nano Lett.* 6 (2006) 2848–2851.
- [13] J.P. Countour, G. Mouvier, *Chem. Phys. Lett.* 33 (1975) 237–240.
- [14] W.M. Lau, *Appl. Phys. Lett.* 54 (1989) 338–340.
- [15] J. Cazaux, *J. Electron Spectrosc. Relat. Phenom.* 105 (1999) 155–185.
- [16] J. Cazaux, *J. Electron Spectrosc. Relat. Phenom.* 113 (2000) 15–33.
- [17] H. Cohen, *Appl. Phys. Lett.* 85 (2004) 1271–1273.
- [18] H. Cohen, O.V. Zenkina, A.D. Shukla, M.E. Van der Boom, *J. Phys. Chem. B* 110 (2006) 1506–1508.
- [19] H. Cohen, S.K. Sarkar, G. Hodes, *J. Phys. Chem. B* 110 (2006) 25508–25513.
- [20] H. Cohen, R. Maoz, J. Sagiv, *Nano Lett.* 11 (2006) 2462–2466.
- [21] A. Vilan, T.A. Bendikov, H.J. Cohen, *J. Electron Spectrosc. Relat. Phenom.* 162 (2008) 99–105.
- [22] J. Cazaux, *J. Electron Spectrosc. Relat. Phenom.*, in press.
- [23] B. Ulgut, S. Suzer, *J. Phys. Chem. B* 107 (2003) 2939–2943.
- [24] F. Karadas, G. Ertas, S. Suzer, *J. Phys. Chem. B* 108 (2004) 1515–1518.
- [25] S. Suzer, A. Dana, *J. Phys. Chem. B* 110 (2006) 19112–19115.
- [26] H. Sezen, G. Ertas, A. Dana, S. Suzer, *Macromolecules* 40 (2007) 4109–4112.
- [27] D.F. Mitchell, K.B. Clark, J.A. Bardwell, W.N. Lennard, G.R. Massoumi, I.V. Mitchell, *Surf. Interface Anal.* 21 (1994) 44–50.
- [28] U.K. Demirok, G. Ertas, S. Suzer, *J. Phys. Chem. B* 108 (2004) 5179–5181.
- [29] G. Ertas, U.K. Demirok, A. Atalar, S. Suzer, *Appl. Phys. Lett.* 86 (2005), Article No.: 83110.
- [30] E. Karabudak, U.K. Demirok, S. Suzer, *Surf. Sci. Lett.* 600 (2006) L12–L14.
- [31] O.L. Curtis Jr., J.R. Srouf, *J. Appl. Phys.* 48 (1977) 3819–3828.
- [32] R.C. Hughes, *Phys. Rev. B* 15 (1977) 2012–2020.
- [33] T. Wang, T.E. Cheng, L.P. Chiang, C.H. Wang, N.K. Zons, C. Huang, *IEEE. Trans. Electron. Devices* 45 (1998) 1511–1517.
- [34] C.J. Kang, G.H. Buh, S. Lee, C.K. Kim, K.M. Mang, C. Im, Y. Kuk, *Appl. Phys. Lett.* 74 (1999) 1815–1817.
- [35] H. Hovel, B. Grimm, M. Pollmann, B. Reihl, *Phys. Rev. Lett.* 81 (1998) 4608–4611.
- [36] M. Marsi, R. Belkhou, C. Grupp, G. Panaccione, A. Taleb-Ibrahimi, L. Nahon, D. Garzella, D. Nutarelli, E. Renault, R. Roux, M.E. Couprie, M. Billardon, *Phys. Rev. B* 61 (2000) R5070–R5073.
- [37] M. Bauer, C. Lei, K. Read, R. Tobey, J. Gland, M.M. Murnane, H.C. Kapteyn, *Phys. Rev. Lett.* 87 (2001), Article No.: 025501.
- [38] G.M. Sessler, R. Gerhard-Multhaupt (Eds.), *Electrets*, 3rd ed., Morgan Hill, 1998.
- [39] L.S. McCarty, G.M. Whitesides, *Angew. Chem. Int. Ed.* 47 (2008) 2188–2207.
- [40] C. Liu, A.J. Bard, *Nature Mater.* 7 (2008) 505–509.
- [41] S. Iwata, A. Ishizaka, *J. Appl. Phys.* 79 (1996) 6653–6713.
- [42] Y. Feldman, A. Zak, R. Tenne, H. Cohn, *J. Vac. Sci. Technol. A* 21 (2003) 1752–1757.
- [43] Y. Hagimoto, H. Fujioka, M. Oshima, K. Hirose, *Appl. Phys. Lett.* 77 (2000) 4175–4177.
- [44] K. Hirose, K. Sakano, K. Takahashi, T. Hattori, *Surf. Sci.* 507–510 (2002) 906–910.
- [45] K. Hirose, *J. Electron Spectrosc. Relat. Phenom.*, in press.
- [46] A.J. Bard, L.R. Faulkner, *Electrochemical Methods*, Wiley, New York, 2001.
- [47] C.M. Dekeyser, S. Biltresse, J. Marchand-Brynaert, P.G. Rouxhet, C.C. Dupont-Gillain, *Polymer* 45 (2004) 2211–2219.
- [48] G. Beamson, D.T. Clark, S.-L. Law, *Surf. Interface Anal.* 27 (1999) 76–86.
- [49] G. Beamson, D. Briggs, *High Resolution XPS of Organic Polymers*, The Scienta ESCA300 Database, Wiley, Chichester, 1992.
- [50] This term is borrowed from the electrochemistry literature and corresponds to the reduced electrochemical voltage (drop) as a result of the incurring current ($V = I \times R$) change.
- [51] A. Schukarev, *J. Electron Spectrosc. Relat. Phenom.*, in press.