TRIBOLOGICAL TRANSFER OF

POLYTETRAFLUOROETHYLENE ONTO SILICON OXIDE

AND POLYMER SURFACES

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IN

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By

Ahmet Uçar

July, 2015

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We certify that we have read this thesis and that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

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ABSTRACT

TRIBOLOGICAL TRANSFER OF POLYTETRAFLUOROETHYLENE ONTO SILICON OXIDE AND POLYMER SURFACES

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M.S. in Chemistry
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July, 2015

The main objective of this study is to understand the nature of tribological transfer of polytetrafluoroethylene (PTFE) onto counter thermally-oxidized silicon, polystyrene (PS), polyvinylchloride (PVC) and poly(methyl methacrylate) (PMMA) surfaces, as well as investigating the possible formation of chemical bonds arising at polymer-semiconductor and polymer-polymer interfaces, while or after tribological material transfer. Tuning the wettability characteristics of PTFE transferred surfaces is also aimed. Within these purposes, first part of the research focused on the preparation of silicon oxide and polymer substrates and the utilization of tribological transfer method in order to form desired PTFE patterns on these surfaces. The realization of this transfer was provided by the design of a simple rig to bring about a friction between the surfaces via sliding a piece of PTFE on silicon oxide and polymer specimens. In order to monitor the tribological interaction in a gradual manner as a function of increasing contact force, a very mild inclination ($\sim 0.5\circ$) along the sliding motion was also employed in some specimens mounted on the inclined aluminum supports. In addition, procedures used to explore the stability of specimens against time and washing / cleaning practices using

various organic solvents and boiling water are given within this part. In the second part of the work, characterization of PTFE-contacted silicon oxide and polymer surfaces was carried out using X-ray Photoelectron Spectroscopy (XPS), Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy and Atomic Force Microscopy (AFM). XPS results were obtained, which revealed that PTFE was faithfully transferred onto the silicon oxide and polymer surfaces upon even at the slightest contact; SEM and AFM images reinforced that stable morphological changes could be imparted onto the counter silicon oxide surfaces. In experiments where the inclined aluminum supports were used to create gradual tribological transfer of PTFE onto counter silicon oxide surfaces, use of relation between the increase in contact force with respect to transferred amount of PTFE helped us to estimate the minimum apparent contact pressure needed to realize the PTFE transfer, which was found to be about 5 kPa. Stability of the patterns imparted towards time and various chemical washing processes lead us to postulate that the interaction was most likely occurred with formation of chemical bonds. Contact angle measurements, which were carried out to monitor the wettability of the silicon oxide surface, showed that upon PTFE transfer the hydrophobicity of the SiO_2 surface could be significantly enhanced, depending on the pattern sketched onto the surface. All of these findings show that tribological transfer of PTFE onto various counter surfaces is possible by a simple procedure, which has both academical and commercial importance.

Keywords: Tribological Transfer, PTFE, XPS, Silicon Oxide, Wettability

ÖZET

POLİTETRAFLOROETİLENİN SİLİKON OKSİT VE POLİMER YÜZEYLERE TRİBOLOJİK TRANSFERİ

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Tez Danışmanı: Prof. Dr. Şefik Süzer
Temmuz, 2015

Bu çalışmanın temel amacı politetrafloroetilen (PTFE)'in termal olarak oksitlenmiş silikon, polisitren (PS), polivinil klorür (PVC) ve polimetil metakrilat (PMMA) yüzeylere tribolojik transferinin doğasını anlamak, bununla birlikte tribolojik madde transferi sırasında ya da sonrasında polimer-yarıiletken ve polimer-polimer arayüzlerinde meydana gelebilecek kimyasal bağ oluşumlarını incelemektir. PTFE'nin transfer edildiği yüzeylerin ıslanabilirlik özelliklerinin düzenlenmesi de amaçlanmaktadır. Bu hedefler doğrultusunda, araştırmanın ilk bölümü silikon oksit ve polimer alt katmanların hazırlanması ve bu alt katman yüzeylerinde istenilen PTFE desenlerinin oluşturulması amacıyla tribolojik transfer yönteminin kullanımı üzerine yoğunlaşmıştır. Bu transferin gerçekleştirilmesi, silikon oksit ve polimer örneklerin üzerinde bir PTFE parçasının kaydırılması suretiyle, yüzeyler arasında sürtünme meydana getiren basit bir ekipmanın tasarlanmasıyla sağlanmıştır. Tribolojik etkileşimin temas kuvveti açısından kademeli olarak artışının gözlemlenmesi amacıyla, eğimli alüminyum plakaların üzerine yerleştirilen bazı örneklerde kayma hareketinin gerçekleştiği yönde çok hafif bir meyil (~0.5◦) uygulanmıştır. Buna ek olarak, örneklerin zamana ve çeşitli

organik çözücüler ve kaynar suyla yıkama / temizleme süreçlerine karşı dayanıklıklarını keşfetmek amacıyla kullanılan prosedürler yine bu bölüm içerisinde verilmiştir. Çalışmanın ikinci bölümünde, PTFE ile temas eden silikon oksit ve polimer yüzeylerin karakterizasyonu, X-ışını Fotoelektron Spektroskopi (XPS), Taramalı Elektron Mikroskobu (SEM), Fourier Transform Infrared (Kızılötesi) Spektroskopi (FT-IR) ve Atomik Kuvvet Mikroskobu kullanılarak gerçekleştirilmiştir. PTFE'nin silikon oksit ve polimer yüzeylere en hafif temasta bile güvenilir bir biçimde geçtiğini gösteren XPS sonuçları elde edilmiş; SEM ve AFM görüntüleri karşı silikon oksit yüzeylere sağlam morfolojik değişikliklerin uygulandığını desteklemiştir. Karşı silikon oksit yüzeylere tribolojik PTFE transferinin kademeli olarak artışı için eğimli alüminyum plakaların kullanıldığı deneylerde, temas kuvvetindeki artışla, transfer edilen PTFE'nin miktarı arasındaki ilişki, PTFE transferini gerçekleştirmek için gereken 5 kPa değerindeki minimum görünür temas basıncının hesaplanması için bize yardımcı olmuştur. Zamana ve çeşitli kimyasal yıkama işlemlerine karşı desenlerin gösterdiği dayanıklılık, etkileşimin yüksek ihtimalle kimyasal bağlarla oluştuğu yönündeki önermemize yol göstermiştir. Silikon oksit yüzeylerinin ıslanabilirlik özelliklerinin izlenmesi amacıyla uygulanan temas açısı ölçümleri, PTFE transferiyle silikon oksit yüzeylerin hidrofobik özelliklerinin, transfer edilen desene bağlı olmak üzere, önemli ölçüde artırılabildiğini göstermiştir. Bulguların tümü PTFE'nin çeşitli karşı yüzeylere tribolojik transferinin basit bir prosedürle mümkün olduğunu, bu transferin de akademik ve ticari anlamda önemli olduğunu kanıtlar niteliktedir.

Anahtar sözcükler: Tribolojik Transfer, PTFE, XPS, Silikon Oksit, Islanabilirlik

Acknowledgement

More than anything and anyone, I owe this life to my parents, Birgül and Süleyman, to whom I did not fear resembling in no circumstances. This and next and next and… will be dedicated to you.

"Don't walk in front of me, I may not follow.

Don't walk behind me, I may not lead.

Just walk beside me and be my friend."

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List of Abbreviations

AES: Auger Electron Spectroscopy

AFM: Atomic Force Microscopy

DCM: Dichloromethane

FT-IR: Fourier Transform Infrared Spectroscopy

HCl: Hydrochloric Acid

HDPE: High-Density Polyethylene

HF: Hydrofluoric Acid

ITME: Institute of Electronic Materials Technology

NaOH: Sodium Hydroxide

PCTFE: Polychlorotrifluoroethene

PE: Polyethylene

PMMA: Poly(methyl methacrylate)

PS: Polystyrene

PTFE: Polytetrafluoroethylene

PVC: Polyvinylchloride

SEM: Scanning Electron Microscopy

STM: Scanning Tunneling Microscopy

TEM: Transmission Electron Microscopy

THF: Tetrahydrofuran

WCA: Water Contact Angle

XPS: X-ray Photoelectron Spectroscopy

Chapter 1

Introduction

1.1. Tribology

1.1.1. Origins of Tribology: Definition and History

As mentioned by Tabor, the word tribology whose roots were based on *tribo* which means *rubbing* in ancient Greek, was recommended in Jost Report to cover the study of friction, lubrication and wear.[1,2] Tribology focuses on the motion of two contacting surfaces from both physical and chemical aspects. It was also defined by Bhushan as *"the art of applying operational analysis to problems of great economic significance, namely, reliability, maintenance and wear of technical equipment, ranging from spacecraft to household appliances."*[3] Since we encounter several actions related to tribology in our daily lives like walking, cooking, writing, driving etc., it is considered as an interdisciplinary study spanning various different disciplines like physics, mechanical engineering, chemistry and materials science.[3] Dowson, in his book named History of Tribology, investigated and pointed out that daily life applications related to tribology were observable even during the Stone Age, where humans used drills to create fire and various bearings were produced for the purpose of pottery and farming.[3], [4] Today, the study of tribology which consists of friction, lubrication, wear and adhesion investigations, holds importance both academically and commercially.

1.1.2. Polymer Tribology: Adhesion, Friction and Wear

Polymers usually have lower friction coefficients as compared to metal and ceramic materials, thus they are used in numerous tribological applications where they slide against the hard materials without using any lubricant.[3] However, before discussing the friction taking place at the interfaces of polymer-polymer, polymer-metal, and polymer-other material surfaces, a thin film which is usually transferred from the polymer onto the other material during the sliding, should be mentioned. In the study of Bahadur published in 2000, a film was observed to transfer from a polymer onto another polymer due to differences in their cohesive energies.[5] In the same work, they had observed that during sliding between metal and polymer surfaces, material transfer was always taking place from polymer to metal. Other studies can also be found in literature, focusing on chemical and physical nature of this polymer adhesion onto the metal surfaces.[6]–[8] The reasons behind the idea that the transfer film formation should be well-defined and understood, in order to control and utilize the friction force arising between the polymer and metal surfaces during sliding. While a polymer is sliding against a metal, the coefficient of friction will probably be different before and after the formation of transfer film, since the self-sliding (polymer-polymer) will occur after the film formation, independently from a metallic substrate, because of stronger interfacial bonding than intramolecular bonds within the bulk polymer.[3]

To summarize, use of polymeric substances is pivotal for industrial applications day by day because lower friction coefficients and decreased wear rates are ever increasingly targeted between contacting materials.

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1.2. Physical and Chemical Characteristics of Surfaces

The complex nature of a solid surface is largely responsible for the interactions, which take place between solid and environment as well as the formation of desired properties different from the bulk of the material. As this nature has a crucial influence on optical, electrical and thermal characteristics, properties of materials with regard to their tribological applications are also determined by these desired properties of the surface. Within this chapter, some related concepts like contacting solid surfaces, adsorption and surface tension/wettability will be briefly introduced.

1.2.1. Solid-Solid Surfaces in Contact

When two solid surfaces are contacted and slid against each other, a junction is created where the material transfer would likely to occur due to the physical or chemical interactions acting on the closest points of asperities, which are involved over surfaces.[9] In addition to the physical interactions resulting from weaker van der Waals forces (London dispersion forces), chemical interactions including stronger bonding (e.g. ionic, metallic, hydrogen and covalent bonding) are also operational. Amount of material transferred from a surface onto the counter surface (previously mentioned as a transfer film formation) is also effected by various conditions like temperature, applied load, shear forces, duration time, contact area and sliding speed.[3], [10], [11]

1.2.2. Physisorption and Chemisorption

Adsorption is defined as "*the process that involves trapping of atoms or molecules that are incident on the surface*" by Somorjai.[12] The atoms or molecules that are adsorbed onto the surface are called adsorbates, while material where adsorption takes place on its surface is called substrate or adsorbent. Bonding occurring between the interface of adsorbate and substrate is stronger than the intramolecular bonds of adsorbed species. Therefore, removing adsorbed molecules from the surface requires an external energy.[3]

Adsorption onto the surfaces is usually explained by two categories; physisorption and chemisorption, as shown in Figure 1. Physisorption usually occurs based on long-range interactions with adsorbates like water vapor, various hydrocarbons, oxygen and inert gases, that might be coming from the environment. This type of adsorption does not involve electron sharing between the surface and adsorbate groups. These molecules might be placed over the surface as monomolecular or polymolecular, with weak van der Waals interactions, thus an energy of about 4-10 kJ/mol is enough to remove these adsorbed molecules from the surface.[3]
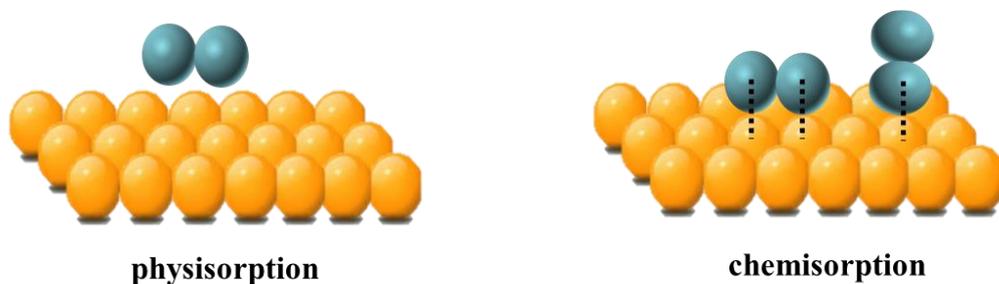
Figure 1. Schematic diagrams of physisorption and chemisorption

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However, when electron sharing between the adsorbate and adsorbent species takes place, stronger but shorter chemical bonding (usually covalent) is formed between these molecules. Compared to physisorption, enthalpies of these interactions are within the range of ~200 kJ/mol.[13] This process is called chemisorption. This amount of energy is comparable with enthalpy of chemical bond formation but the main and important difference between the chemical bond formation process and chemisorption is the limitation of chemisorption to a monolayer adsorption.[3]

1.2.3. Surface Energy, Surface Tension and Wettability

Wetting is briefly described as the interaction between a liquid and a solid, and wettability, that is usually pictured by a sessile/resting droplet as illustrated in Figure 2, is the ability of a solid surface to be wetted/spread with a liquid.[14] When a liquid is dropped onto a solid surface, a recognizable angle arises due to the competing of adhesive forces taking place among liquid-solid interfaces, with cohesive forces acting within liquid molecules. Stronger adhesive forces might provide solid to be wetted with liquid molecules. Lower contact angles indicate that the wettability of the surface is achieved thus the surface is called hydrophilic. Surfaces with higher contact angles are called hydrophobic.
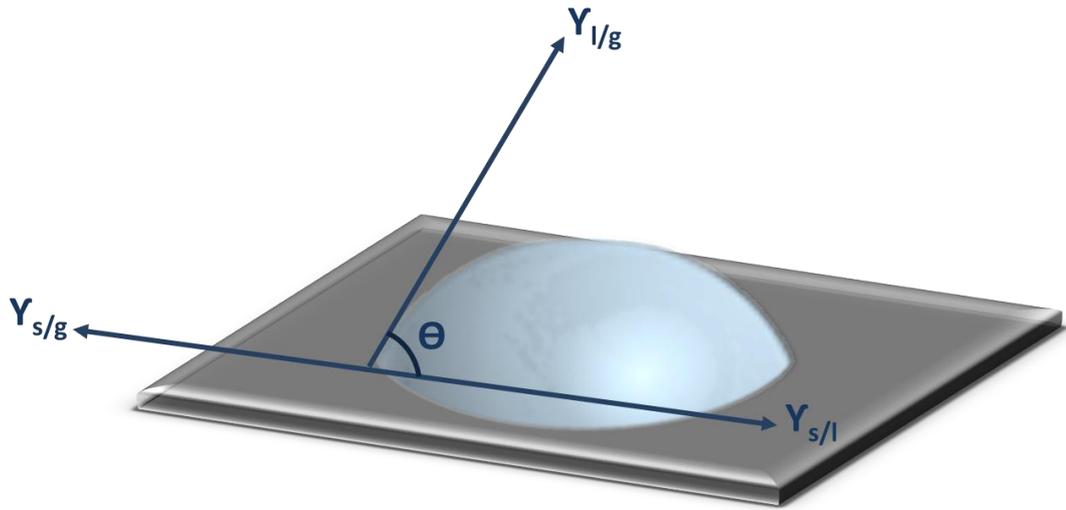
Figure 2. A sessile drop on a solid surface

Surface tension can be defined as the energy which is needed in order to create a unit area of each of the interface, which are designated as solid – gas ($\gamma_{s/g}$), solid – liquid ($\gamma_{s/l}$) and liquid – gas ($\gamma_{l/g}$), as illustrated also in Figure 2.[13] According to this notation, the Young equation is written as;

$$\gamma_{s/g} = \gamma_{s/l} + \gamma_{l/g} * \cos \theta \tag{1}$$

which can also be converted to;

$$\cos \theta = \frac{\gamma_{s/g} - \gamma_{s/l}}{\gamma_{l/g}} \tag{2}$$

and related with the work of adhesion per contact area ($W_{ad} = \gamma_{s/g} + \gamma_{l/g} - \gamma_{s/l}$)

$$\cos \theta = \frac{W_{ad}}{\gamma_{l/g}} - 1 \tag{3}$$

according to Atkins.[13] Therefore, if the contact angle degree is below 90°, work of adhesion per area increases and liquid spreads over the surface. However, at higher contact angles work of adhesion for the liquid decreases that leading to a decrease in wettability.

Although there are several methods to measure contact angle, telescope-goniometer technique, which is also employed in our measurements, is the most widely used to measure the tangent of the angle on a sessile drop, due to its simple utilization and minor requirements, like smaller liquid amount and specimen surface area, etc.

1.3. Polytetrafluoroethylene

Synthesis of a fluorinated and saturated organic compound, polytetrafluoroethylene (PTFE), from a monomer, tetrafluoroethylene by free-radical polymerization, was first reported by Plunkett at DuPont.[15],[16] (See Figure 3) It is a highly chemically-inert substance, with high molecular weight and linear crystalline structure. As in the majority of fluorocarbons, well separation of dipoles between carbon and highly-electronegative fluorine resulted in very strong C-F bonding in PTFE. This leads to significantly high thermal and electrical insulation, hydrophobic characteristics, strength, toughness and low friction coefficients in a large temperature range.[17]–[19]

Due to these desirable properties, PTFE has been heavily used in applications as machine parts, gaskets and nonstick cooking utensils, as mentioned by Stevens.[20]
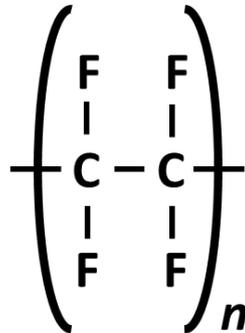
Figure 3. Chemical structure of polytetrafluoroethylene

1.3.1. Tribological Applications

Since PTFE was known to exhibit lower friction coefficients compared to other solid polymeric materials, understanding the physical and chemical nature of tribological interactions occurring at interfaces between PTFE and other solid materials have been academically and commercially important over the last 5 decades. [16], [21], [41]–[49]

Makinson and Tabor's study focuses on the transfer and friction of polytetrafluoroethylene (PTFE) which was slid on glass surfaces, and their characterization using optical and scanning electron microscopy techniques, where they verified the PTFE transfer onto other surfaces during sliding motion. This work was highly significant as an example of the leading research on this field.[21] Also

two frictional regimes named as low and high, changing with both temperature of the environment where the sliding motion was processed, and the sliding speed, were analyzed within this work. In the low-friction regime, defined to be operative at low sliding speeds and/or high temperature, PTFE films with thicknesses varying from 10 to 40 nm, were verified to have transferred onto the counter glass surface. The work was extended to include various thermoplastic polymers such as commercial copolymers of fluorinated ethylene propylene, polychlorotrifluoroethylene (PCTFE), polyethylene (PE), polystyrene (PS), poly(methylmethacrylate) (PMMA), and polyvinylchloride (PVC), and their tribological transfer onto counter clean surfaces.[22]

As an example to the use of different characterization technique, Auger Electron Spectroscopy (AES) was utilized in the work of Pepper where the interaction of PTFE, PCTFE and PVC with various surfaces was monitored.[23] The transfer of a continuous and uniform PTFE film with a thickness of about 2-4 atomic layers onto the metal surfaces was confirmed in this work. However, this was not the case for PVC where any uniform film could not be observed as a result of this sliding, just the chlorine chemisorbed onto the surface. Besides, PCTFE produced chemisorbed chain fragments on the counter metal surface.

In addition, X-ray photoelectron spectroscopy (XPS) was also used to study the tribological interaction of various metals and metal oxides with PTFE.[24], [25] Various materials grown on tribologically transferred-PTFE/glass surfaces was shown to result in markedly higher orientation levels of thin films in the study of Wittmann and Smith.[26]

In literature, several studies can also be found, related to the effect of temperature, sliding speed and applied load on the tribological PTFE transfer onto various surfaces. A brief summary can be given as follows; (i) temperatures are above 150 °C, at which Teflon softens, and (ii) pressures are within the 0.1–10 MPa, and (iii) sliding speeds are in the range of 0.1–10 mm/s.[27]–[30] Furthermore, it is also possible to encounter studies most of which were focused on the investigation of physical properties in order to achieve lower friction coefficients and rates of wear.[31]–[40] However, the scope of our study is not on improvements of the mentioned physical properties whose chemical nature was not fully understood at the atomic scale yet, but to focus on the nature of interaction between polymer and polymer-coated or non-coated silicon oxide surfaces, that are contacted in relative motion.

Computational chemistry methods were also used as powerful tools for the analysis of the mechanism behind friction and formation of transfer films. Onodera's studies that focused on the effect of ionic bonding on tribological film formation between PTFE and aluminum oxide surfaces, can be given as an example.[41], [42] They also worked on the influence of changing environmental conditions on the formation of transferred films in their study. Furthermore, in a recent work of Junk et al., a mechanism leading to the formation of a transferred film of PTFE which was slid over a counter steel surface was offered.[43] According to them, while the sliding is taking place, perfluoroalkyl radicals are formed via mechanochemical scission of C-C bonds of PTFE, due to the difficulty of entire chain transfer, because PTFE has a high molecular weight. In ambient

conditions, perfluoroalkyl radicals react with oxygen to produce peroxy radicals which are then stabilized with formation of acyl fluoride as end groups. After the carboxylic acid groups are created with hydrolysis in humid environment, strong adhesion of PTFE to the counter metal surface is provided by chelation of these carboxylic acid groups. Their findings provide strong chemical evidences to tribological transfer of PTFE onto silicon oxide surfaces.

1.3.2. Hydrophobic Properties

In addition to wide use of PTFE on tribological applications especially due to its low friction coefficient, it also offers a significant potential for altering wettability of surfaces owing to its low surface energy. In low surface-energy materials, wetting characteristics of monolayers is likely to be changed with chain conformation of molecules and type of atoms located at and near the surface. It was reported that repellency with respect to groups located over the surface decreased in the order of $-CF_3 > -CF_2 > -CH_3 > -CH_2$ because of the increasing surface density and not changing force fields, explaining the fact that the wettability of PTFE which includes CF_2 groups is poor as compared to other hydrocarbons.[14] Besides, the hydrophobic nature of PTFE is known to be related with its longer chain length compared to other branching polymers. Therefore, increasing the surface hydrophobicity using PTFE is convenient and has been the subject of many studies, using plasma treatment[44], controlling surface roughness[45], coating[46]–[48] and microfabrication, etc.[49]

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1.4. Characterization Techniques

1.4.1. X-Ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is a commonly used technique for characterization of surfaces with an outstanding surface and chemical selectivity. As a very comprehensive analysis technique, it is also able to provide valuable qualitative and quantitative information in the sense of chemical structure of surface moieties.[50], [51]

As depicted in Figure 4, in XPS, kinetic energy of photoelectrons, which are emitted from the core levels of a sample by high-energy X-ray radiation, are measured via the electron spectrometer and data is represented as a plot of intensity versus binding energy of specific elements.[52] Most common energies of X-ray photons typically used in commercial instruments are 1253.6 eV for Mg Kα and 1486.6 eV for Al Kα. The kinetic energy which is experimentally measured by the electron energy analyzer is based on the energy of these incoming photons, as determined by the relationship;

$$E_B = h\upsilon - E_K - \Phi \qquad (4)$$

where E_B is the binding energy of the photoelectrons which are emitted, $h\upsilon$ is the energy of incoming photon, E_K is the kinetic energy of the photoelectron and Φ is the work function which is specific to instrument and thus useful for avoiding probable systematic errors.[52] Since all the parameters except the binding energy

of the photoelectrons are known, it can easily be calculated with this relationship and represented as a spectrum as shown in Figure 5.
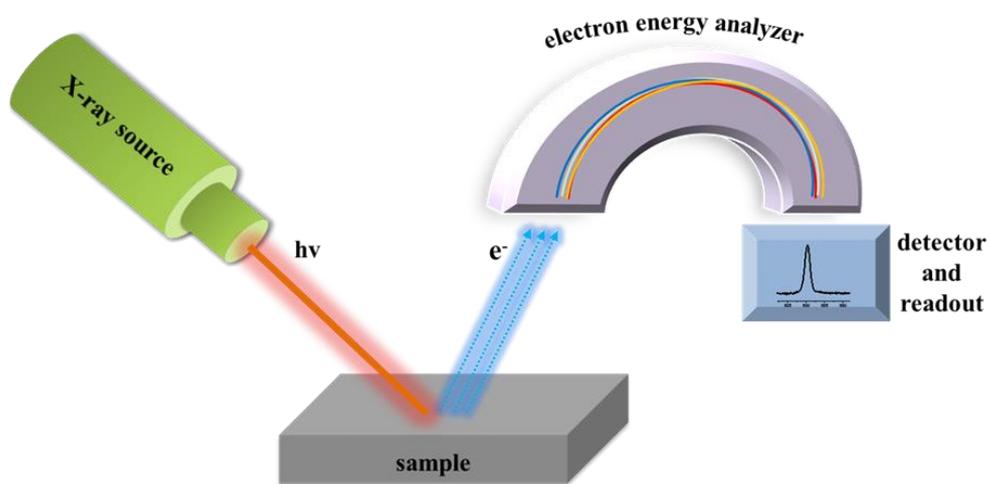
Figure 4. Schematic representation of the XPS
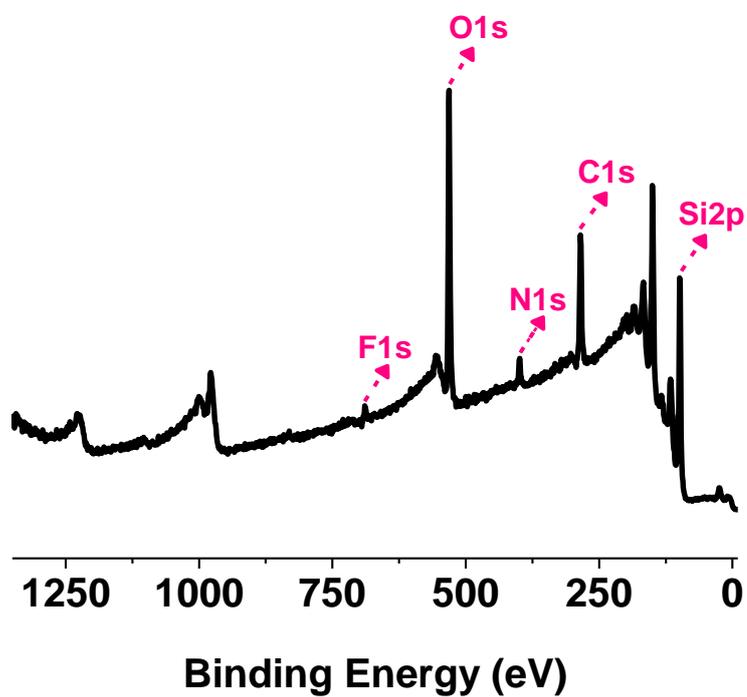
Figure 5. A typical XPS survey spectrum

XPS can supply crucial chemical information about the surfaces, since chemical state of an atom affects the energies of core levels where photoelectrons are emitted from. Chemical state depends on the chemical environment i.e. electronegativity of ligands that an atom is bonded to. A change in the oxidation state of an atom for instance, can be monitored by a shift of usually about 0-3 eV in the corresponding binding energy. The shifts in C1s binding energy of fluorinated hydrocarbons can be given as an example, as shown in Figure 6. Increasing oxidation state of the carbon atom due to the increase in the number of bonded fluorine atoms, leading to shifts to higher binding energies. While C-H groups are usually observed around 285 eV, C-F, C-F$_2$ and C-F$_3$ groups are observed at ~289 eV, ~292 eV and ~293 eV, respectively.[53] Thus XPS spectra also supply information about the chemical states and atomic orbitals, in addition to the elemental specificity.[50]
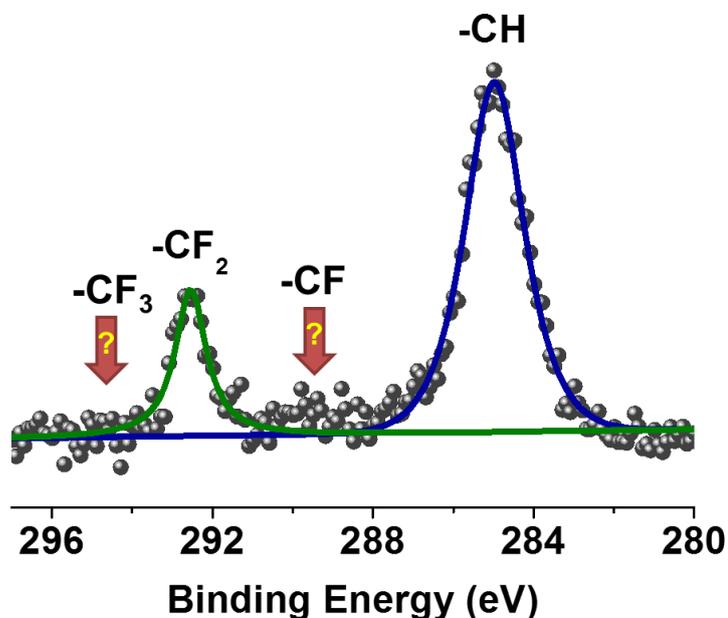
Figure 6. C1s region of XPS spectrum showing chemical shifts in fluorinated hydrocarbons

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Surface sensitivity of XPS results mainly from the short mean free path of electrons. Inelastic mean free path (λ), is defined as an average distance traveled by an electron in between two collisions.[54] Although highly energetic X-rays are able to penetrate through the sample in micrometer levels, ejected photoelectrons can only be obtained from the surface depths lower than 10-12 nm, because photoelectrons usually incur losses when ejected from larger depths. They make inelastic and elastic collisions that cause their kinetic energies to decrease. This leads to ~95% of information loss when surface depths are higher than ~10 nm, as demonstrated in the Figure 7 and the relationship is given by the Beer-Lambert law;

$$I = I_0\, e^{(-d/\lambda)}$$
(5)

when I_0 is the incident intensity, I is the intensity of the emitted photoelectron and d is the depth length which the photoelectron is emitted from, and λ is the mean free path.
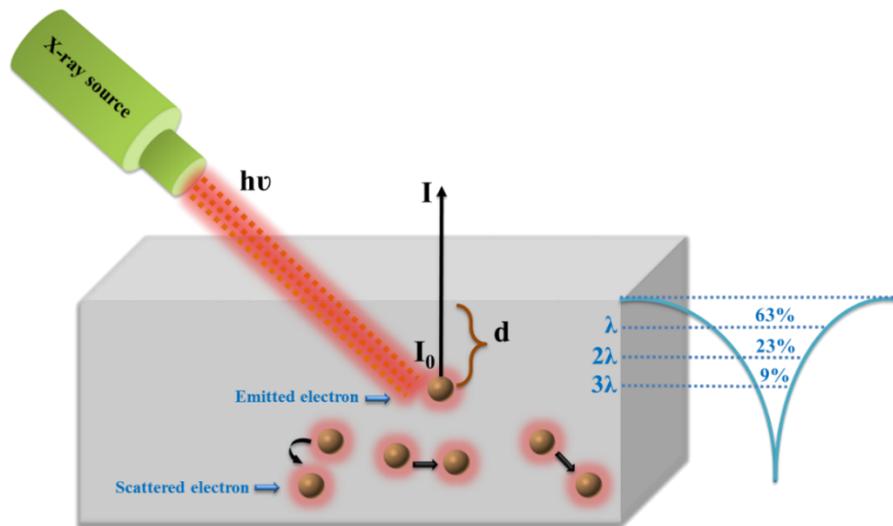
Figure 7. Schematic representation of the photoelectric effect and attenuation length of emitted photoelectrons

In addition, estimation of film thicknesses can be utilized by XPS using the Equation 4, the measured differences between initial and final intensities, and the Beer-Lambert relationship. For instance, thickness of thermally oxidized over layer of silicon surfaces can be estimated from intensity ratio of obtained Si 2p peaks using this formula;

$$I_{SiOx} / I_{Si} = [1 - e^{(-t/\lambda)}] / e^{(-t/\lambda)} \tag{6}$$

where I_{SiOx} and I_{Si} are the intensities of Si 2p peaks obtained from the oxide layer (Si^{4+}) and the Si (Si^0) environment, respectively. t is the thickness of oxide overlayer and λ is the inelastic mean free path (attenuation length) of electron in the oxide layer, which is taken as 3 nm.[55] According to these parameters, we can estimate the oxide layer thicknesses of our silicon oxide specimens. As illustrated in Figure 8, the oxide layer in Specimen-1 was estimated to be ~4 nm and for Specimen-2, this increased to ~10 nm.
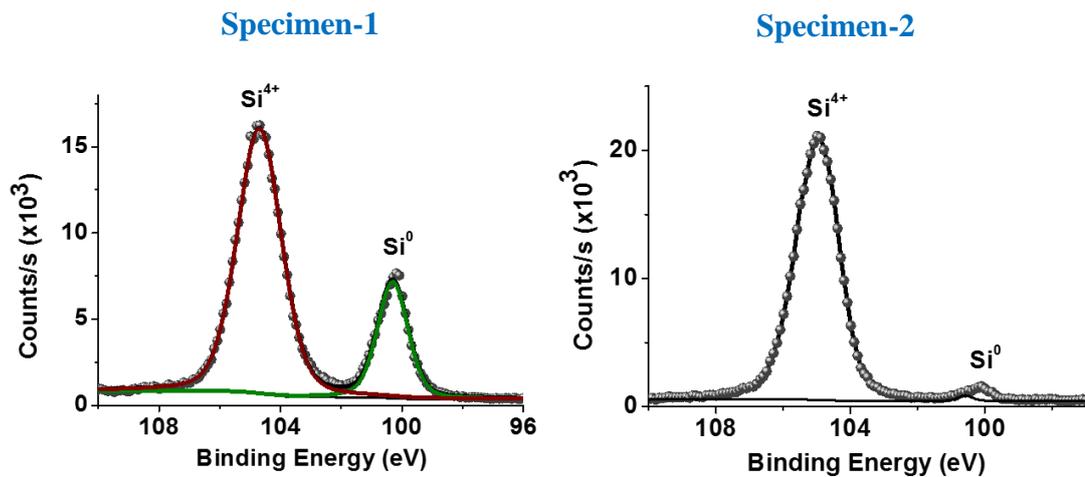
Figure 8. Si 2p spectra obtained from two different specimen surfaces

Apart from these valuable advantages, there are also some charging-related problems leading to shifts in binding energies, which one somehow needs to overcome, while carrying out an XPS measurement. If the sample to be analyzed is non- or poor-conductor like most of the polymeric species, the positive charges on the surface of the sample created after emission of photoelectrons, could not be compensated with ease in contrast to conducting samples. In these circumstances, flood gun is used that provides low-energy electrons to neutralize the sample and compensate these unwanted shifts in energies.

Moreover, the requirement of ultra-high vacuum environment, needed to prevent photoelectrons from scattering before reaching the spectrometer, still remains as another significant challenge for XPS measurements, although recent studies where ambient-pressure XPS is carried out as the main characterization technique can also be found in literature.[56]–[58]

1.4.2. Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) is a high-resolution imaging technique for physical characteristics of surfaces. In this technique, high-energy electron beam is sent to the surface of a specimen to excite atoms which then emit secondary electrons. These secondary electrons are collected by SEM and an image which gives information about morphology of the specimen surface is created. In addition to the detection of secondary electrons which are generally surface sensitive, back-scattered electrons which provide valuable information about bulk of the specimen, are also detected by SEM.[59] Due to its high-resolution and

convenience on surface imaging as well as rapid scan opportunities, SEM is very useful for tribology studies.[60]

For SEM measurements, there is also a need for high vacuum of about 10^{-6} torr or lower, like most of the analysis techniques involving electrons. The other requirement for these measurements is that the sample to be analyzed should also be electrically conductive in order to avoid loss of images that may probably occur due to charging on the surface. Although there are various methods to also characterize insulator materials, other problems like thermal degradation and radiation defects might be encountered more in nonconductive samples than in conductors.[61]

1.4.3. Fourier Transform Infrared Spectroscopy (FT-IR)

Infrared Spectroscopy is a powerful technique for characterizing almost all organic and inorganic materials since most absorb infrared radiation.[61] Since each molecule consists of a combination of bonded atoms, frequencies of vibrations of the bonds created by these atoms lead to fingerprint spectra of molecules. Therefore, infrared spectroscopy can be used as a powerful tool for qualitative analysis. In addition, semi-quantitative information can also be obtained using peak intensity/area, according to the well-known Beer's Law;

$$A = \varepsilon * b * c \qquad (7)$$

where A designates absorbance, ε the constant of molar absorptivity, b is the path length of the absorbing medium and c is the concentration of the absorbing

species.[61], [62] The new FT-IR Spectrometers provide fingerprint identification of all organic and inorganic molecules, apart from some homonuclear molecules, with high-sensitivity and resolution in very short times.[63]

1.4.4. Atomic Force Microscopy (AFM)

After the invention of Scanning Tunneling Microscopy (STM) which is able to provide very high-resolution morphological mapping of electrically conductive surfaces, Binnig *et al.* developed a new technique called Atomic Force Microscopy (AFM) in order to investigate both conductive and insulator surfaces on the nanometer-scale.[64] The working principle of AFM is similar to STM, except that the force arising between a tip and the surface is sensed instead of the tunneling current as in STM. In contact-mode AFM measurements, the sample is placed on the stage and cantilever is brought into light contact with the surface of the sample. The stage is fabricated from piezoelectric materials that converts electrical signals into mechanical stress. The vertical deflection created on the cantilever is sensed with a laser beam which is sent to the cantilever vertex and read by four quadrants of a photodetector.[3] There is also a non-contact mode of AFM measurements where the tip is approached to the surface closely but not touched it, which is an advantageous feature especially in the area of biological applications, in order to avoid surface damage.[65] AFM is a highly surface sensitive technique and produces topographic imaging at micro and nanometer-scale and even atomic scales, with many useful applications within tribology.[66]–[68]

1.5. Aim of the Present Study

This study will mainly focus on investigating the physical and chemical nature of the polymer-semiconductor and polymer-polymer interactions that are tribologically created while a PTFE tip is slid over non-coated and PMMA/PVC/PS-coated thermally oxidized silicon samples.

In Chapter-2, experimental section, preparation of silicon oxide substrates, coating of these surfaces with various polymers, procedure of creating tribological interaction between PTFE and coated / non-coated surfaces in a gradual as well as non-gradual manner will be given. Gradual tribological interaction refers to increase of material transfer with respect to direction of sliding motion. Samples on where the gradual transfer is used, will be utilized to determine the onset point, where the interaction between contacted surfaces begins, and apparent contact force and pressure arising at this onset. In order to assess durability of the created features, non-gradual PTFE transfer procedure onto samples will be employed and various cleaning / washing methods on their surfaces will also be included within this chapter.

Chapter-3 will give the results and related discussion on use of several characterization techniques like X-ray Photoelectron Spectroscopy, to monitor the chemical and physical changes that has occurred on the surface of specimens and further analysis made for understanding the nature of this interaction. Other investigations using Atomic Force Microscopy and Scanning Electron Microscopy to reveal morphological alterations appearing after PTFE sliding will be reported.

In addition, Contact Angle Measurements used to monitor the wettability of surfaces will be provided and discussed.

Finally, in the appendix part of the thesis, results showing the effect of various factors (i.e. different counter substrate, application of chemical treatments) on the nature of this interaction will be presented.

Chapter 2

Experimental

2.1. Materials

Si (100) wafers which were n- or p-doped and with an electrical conductivity of ~20 Ω-cm were purchased from the Institute of Electronic Materials Technology (ITME) via www.universitywafer.com. Glasses that were used as substrate in some experiments, were obtained from ISOLAB microscope slides. The PTFE tip was cut out from a larger general-purpose PTFE sheet which has a thickness of about 1 mm and employed in all sliding experiments. Its purity was checked with FT-IR and XPS techniques. Poly(methyl methacrylate) (PMMA), poly(vinyl chloride) (PVC), Polystyrene (PS), Chlorobenzene, Hydrochloric Acid (HCl) and Sodium Hydroxide (NaOH) were purchased from Aldrich. Hydrofluoric Acid (HF), Toluene, Dichloromethane (DCM), Tetrahydrofuran (THF), Acetone and Ethanol were obtained from Merck. Dimethylformamide was purchased from the Honeywell Riedel-de Haën. All these chemicals were used without any further purification. Deionized water used in the entire experimental process was obtained from a three-stage Millipore Milli-Q Synergy 185 purification system.

2.2. Instrumentations

An X-Y-Z stage (see Figure 9) which was purchased from Nanomagnetics Instruments Ltd. allowed us to induce micrometer-scale-motion in 2D and as such, was used to slide the fabricated PTFE tip over coated / non-coated silicon oxide surfaces. Approach of the PTFE tip onto the counter surface in z-axis was monitored with an optical microscope.
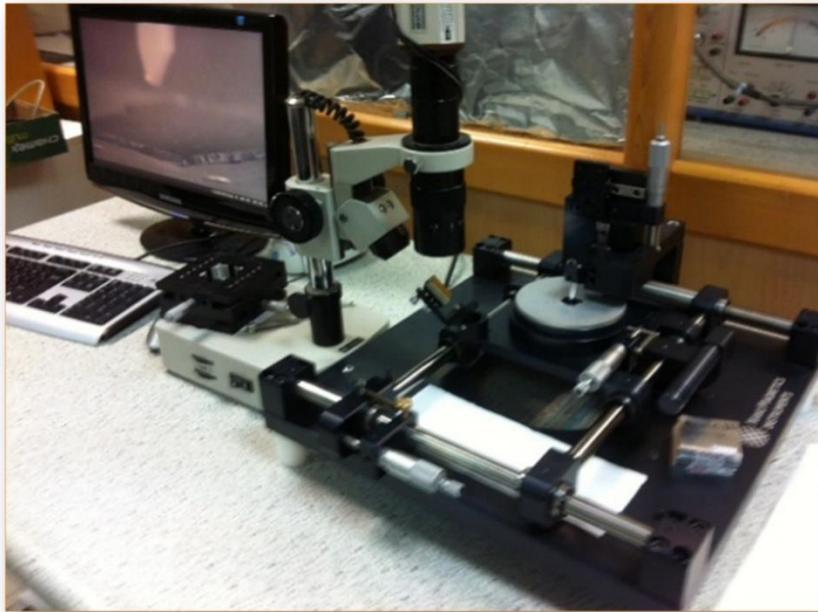
Figure 9. Optical microscope attached x-y-z stage used for the sliding experiments

Motions were optimized and controlled with a computer software, *NMI Motor.* Instrument is able to create motions in a range of ~7 cm in both x and y directions, with steps of 25 µm or higher. After the specimen to be slid with PTFE is placed on the stage, the PTFE tip is approached onto the surface manually while

the distance between the tip and counter surface is monitored with the optical microscope, as illustrated in Figure 9. For specimens on which non-gradual tribological interaction is processed, tip is contacted with the surface until a deflection of the tip is seen. On surfaces of specimens on which gradual tribological transfer would be processed, tip was approached onto the surface as close as possible, but not touched. The reason is that the determination of the point that we defined as onset point, (where tip is touched and interaction begins), is of significance to us for estimating the contact force and the pressure enabling the interaction. In order to create this gradual interaction between contacted surfaces in motion, inclined aluminum platforms were used as support under the silicon oxide surfaces. (See Figure 10)
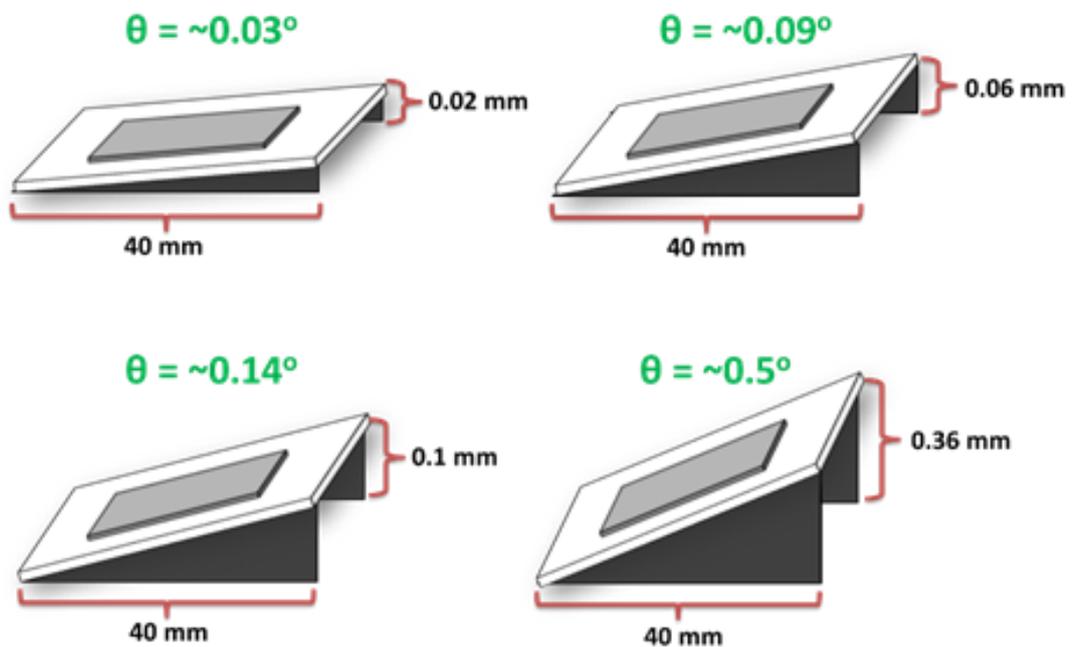
Figure 10. Aluminum supports with different inclination angles

These platforms had different inclination angles (i.e. ~0.03º, ~0.09º, ~0.14º and ~0.5º). When they were used as support under the silicon oxide surfaces, the contact force and the pressure increased continuously after the onset point. This increase in the contact force and pressure caused also the material transfer to increase gradually in the direction of sliding. These gradual increases directly depend on the inclination angles of the platforms, which were designed and fabricated by Dr. Şakir Baytaroğlu from the Department of Mechanical Engineering, Bilkent University. In order to follow the gradual interaction easier, the aluminum support with the highest inclination (0.5º) was usually used in our experiments.

FT-IR spectra of the samples were collected using a Bruker Tensor 27 spectrometer in the range of 4000-400 cm^{-1}, with a resolution of 4.0 cm^{-1}. Scan numbers and velocities of the moving mirror were optimized, depending on the signal to noise ratio of the spectrum. All silicon wafers used for FT-IR measurements were highly transparent to infrared radiation.

Surfaces of specimens were monitored using a Zeiss Evo 40 Scanning Electron Microscope which was operated at 15 kV, under a high-vacuum of approximately 3 x 10^{-7} mBar. Silicon wafers to be analyzed were attached to the aluminum sample holders using conductive carbon tapes.

As a complementary technique to SEM measurements, AFM measurements were carried out under ambient conditions in order to characterize the morphology as well as the structure of the surfaces. An AFM instrument (Nanomagnetics Instruments - ambientAFM) was used to map the topography in the contact mode

using silicon cantilevers. *SPM Ambient* computer software was used for data processing and analysis.

Hydrophobicity/wettability of surfaces was determined with a Tantec CAM-Micro Contact Angle Meter. The image of droplets were examined with the aid of an optical microscope.

For chemical analyses of the specimen surfaces, a Thermo Fisher K-alpha electron spectrometer having a monochromatic AlKα X-ray photon source with an energy of 1486.6 eV was utilized. The spectrometer can probe the surfaces with various X-ray spot sizes that can be changed from 30 µm to 400 µm. A flood gun operated as neutralizing electron source, is used in cases where some unexpected shifts in binding energy were encountered due to the significantly lower electrical conductivity of polymer coated samples, in order to compensate the charging. As illustrated in Figure 11, three different scanning modes were utilized in order to carry out the chemical analyses. The first mode is commonly known as point scan, where a spectrum is recorded at a single spot between determined intervals of binding energies. The second mode is the line-scan analysis including individual point scans along a designated line and step size between consecutive points. The third one is the aerial two dimensional spectral mapping which is recorded in the snap-shot mode that is the most advantageous way of collecting a large number of spectra in a short time, although the spectral resolution is lower.
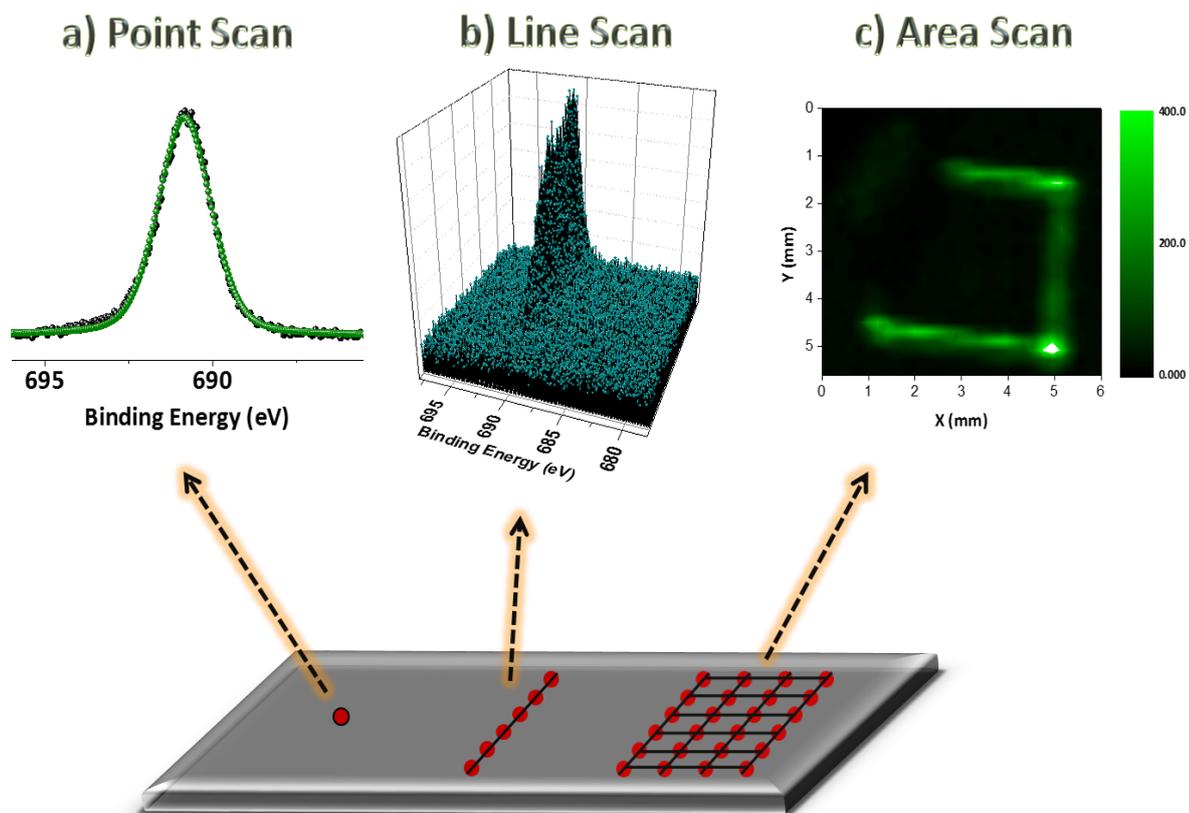
Figure 11. XPS modes performed for the surface characterization of specimens: (a) point scan, (b) line scan and (c) area scan

2.3. Procedures

2.3.1. Preparation of Polymer-Coated and Non-Coated Silicon Oxide Surfaces

Commercially available silicon wafers were cleaned with aqueous HF solution for ~30 s in order to etch away the native oxide layer. Then they were washed with deionized water and dried with nitrogen flush. This step was repeated three times. Afterwards, specimens were annealed in air at 700 $^{\circ}$C for 3 hours to grow approximately 4 to 10 nm-thick oxide layers. Estimation of oxide over layer thickness was briefly mentioned within the Section 1.4.1.

In separate experiments, effect of surface treatment were tested by dipping the samples into aqueous solutions of 1M HCl or NaOH for an hour. Afterwards, all samples were soaked in deionized water for an additional hour. Homogeneous polymer coatings onto silicon oxide wafers were achieved using the spin coating process (See Figure 12) in different spin velocities, varying from 1500 rpm to 2500 rpm depending on the intended film thickness, using polymer solutions which are PMMA (2% w/w in toluene), PVC (2% w/w in THF) and PS (2% w/w in THF).
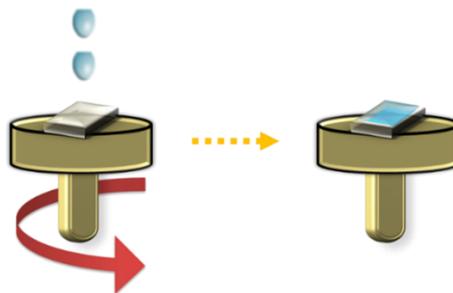
Figure 12. Schematic representation of spin-coating process

2.3.2. Creating Tribological Interaction in a Gradual / Non-Gradual Manner

As mentioned in previous sections, for a gradual tribological transfer of PTFE onto counter non-coated silicon oxide surfaces, a small inclination of ~0.5∘ along the sliding motion was applied using fabricated inclined aluminum platform as the support, as shown in Figure 13. The purpose of the gradual tribological transfer was to determine the onset point and the contact force / pressure which is needed for initiation of material transfer from PTFE onto the counter silicon oxide surface. In order to realize this, PTFE tip was slowly approached onto the surface, without touching. We did not contact the PTFE tip onto the surface initially, because we wanted that touching and corresponding interaction to start after travelling some distance. In this way, we targeted to determine whether the interaction between surfaces begins at the moment when PTFE is touched, or later. Use of inclined support placed under silicon oxide, provided gradual increase in the contact force / pressure as well as in the material transfer, during sliding motion. Finally, monitoring the increase in intensity of the peak corresponding to material transfer via XPS, is expected to provide information related to the position of the onset. After the determination of this position, the contact force and pressure arising on this onset was estimated using the procedure which will be given in the next section.

On the other hand, for specimens not to be analyzed in this gradual manner, aluminum support was not attached. An optimum speed of the X-Y stage was chosen as ~1 mm/s while performing sliding experiments for all the processes under

ambient conditions. The tip is cleaned with acetone and nitrogen flush after each experiment.
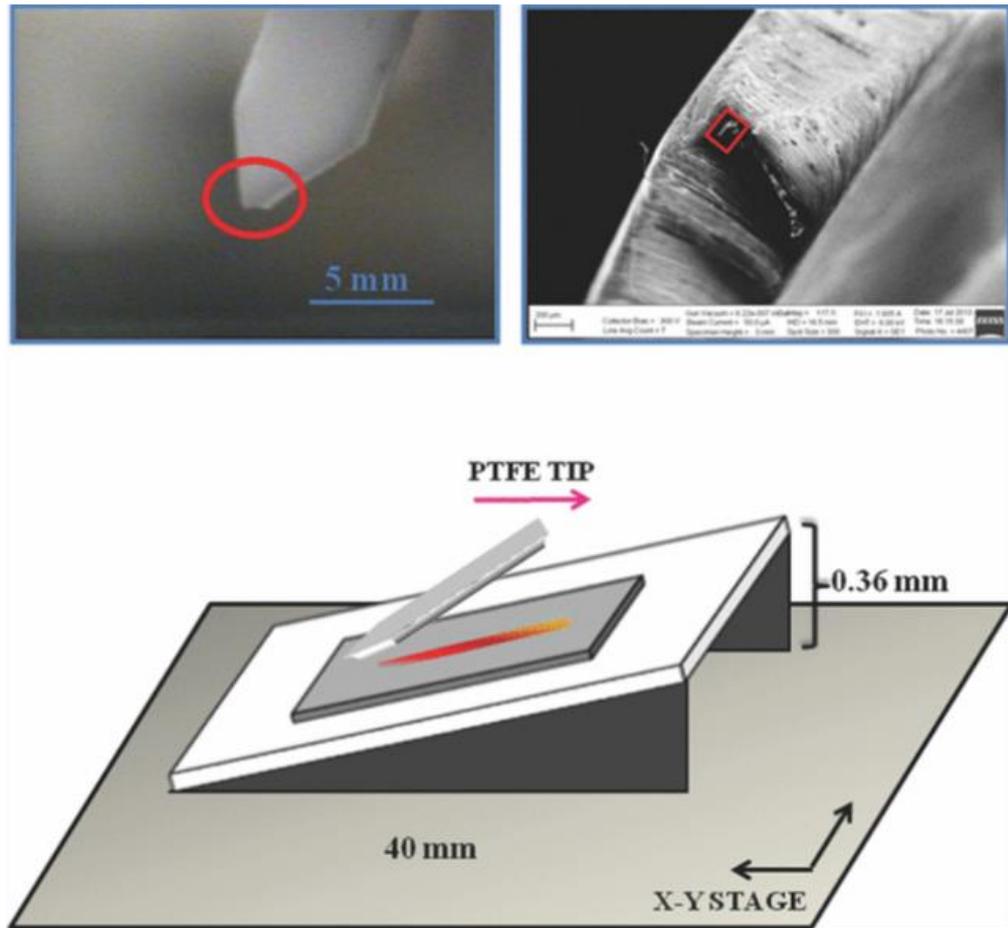
Figure 13. A schematic representation of the rig used to bring about gradual tribological interaction between PTFE tip and silicon oxide surface. Optical and electron microscope images (upper left and right, respectively) of the PTFE tip are also presented. The apex of the tip is highlighted with a red rectangle. "Reproduced with permission from J. Chem. Phys. 141, 164702. Copyright 2014, AIP Publishing LLC."

2.3.3. Estimation of Minimum Apparent Contact Force and Pressure Enabling Tribological Transfer

In order to realize an interaction between the PTFE and silicon oxide in sliding motion, a contact force or pressure should be exerted onto the silicon oxide surface. To estimate this minimum contact force and related apparent contact pressure needed to enable this interaction, firstly an onset point where the interaction between contacted surfaces begins, was determined. The reason for this is that the contact force and pressure arising on this onset will be minimum values needed to initiate this transfer. In our work, this determination was made monitoring changes in F1s intensity of scans taken along a scratched PTFE line on a sample on which the gradual transfer was utilized.

After the determination of the onset point, the deflection of PTFE tip was related with the transverse force exerted on the apex of the PTFE tip during sliding, as illustrated in Figure 14. During sliding the PTFE tip is continuously moved upwards thus the contact force exerted on the apex of the tip increases with deflection of PTFE tip leading to the gradual increase in PTFE transfer as observed in XPS measurements. The deflection of PTFE tip was calculated using geometrical similarity between two triangular-like shapes; first of which was aluminum inclined support whose all dimensions are known and the second one is the elastic deflection of PTFE tip which is shown in Figure 14. Because PTFE tip was approached onto the surface with an angle of ~45° and lengths of its edges are known except the deflection which was considered as third edge, all dimensions can be estimated.

Then, the standard elastic beam deflection formula[69] was used to relate these parameters;

$$P = \frac{3\,E\,I}{L^3}\,\delta \qquad\qquad (8)$$

where P is the transverse force, δ is the deflection of the PTFE tip, I is the moment of inertia of the tip around bending axis which can be calculated knowing the dimensions of the PTFE tip (thickness: 1 mm, width: 5 mm, length, L: 37 mm) and E is the elastic modulus (Young's modulus) of the PTFE tip which is 0.5 GPa .[70] In order to calculate the pressure between surfaces after the force was estimated, SEM images of the PTFE tip were used as a reference for the apparent contact area. The PTFE tip used is depicted with; (a) optical and (b) electron microscope images (respectively on the upper part of the Figure 13).
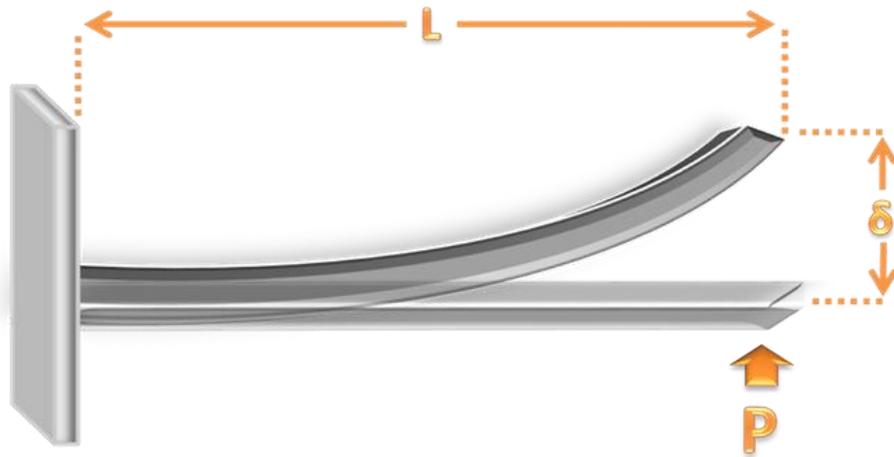
Figure 14. Schematic illustration of beam deflection when the pressure is exerted on the apex of tip

2.3.4. Controlled Transfer of PTFE Patterns onto Counter Surface

X-Y stage was not only used to create individual lines by sliding, but it was also used to control the tribological PTFE transfer with respect to changes in pattern density and creation of designated molds, as displayed in Figure 15. Also, on some samples to be analyzed after washing / cleaning processes, a square shape was implemented. Furthermore, a pattern in the shape of 'bil uni' (abbreviation of Bilkent University) was also imparted onto another specimen.
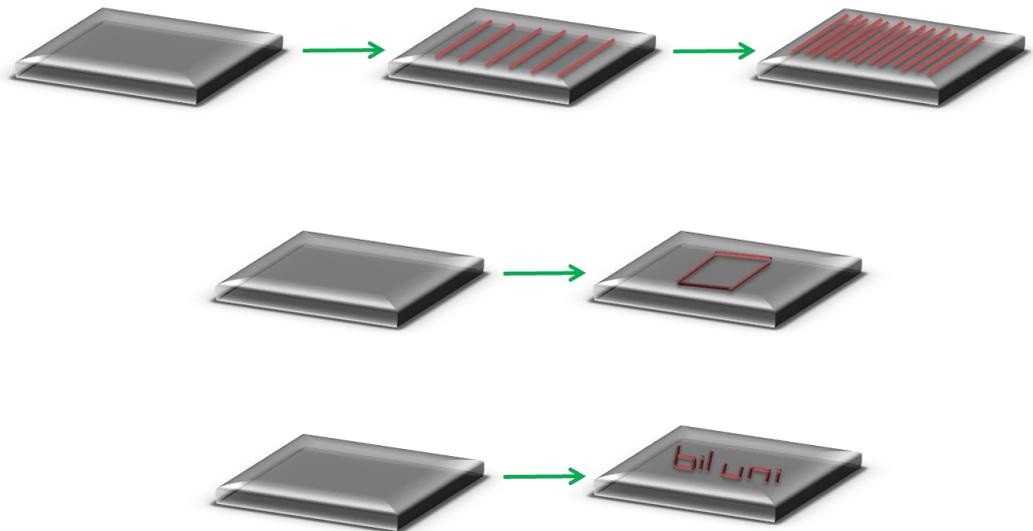
Figure 15. Implementation of several individual lines onto the counter silicon oxide surface by sliding with PTFE

2.3.5. Washing / Cleaning Processes of PTFE Transferred Surfaces

The aim of implementing washing / cleaning processes to PTFE transferred surfaces was to understand the nature of tribological interaction, by monitoring durability of the materials transferred. In our case, durability of transferred PTFE residues against time and with respect to chemical treatments were tested. For the test of durability against chemicals, a sample on which a square shape scratched as mentioned before, was exposed to several washing / cleaning processes with various organic solvents, (i.e. acetone, ethanol, THF, DCM, toluene) each in ultrasonic bath for 10 minutes. (See Figure 16) Samples were then cleaned with deionized water and dried with nitrogen flow. XPS measurements were employed after each cleaning treatment.
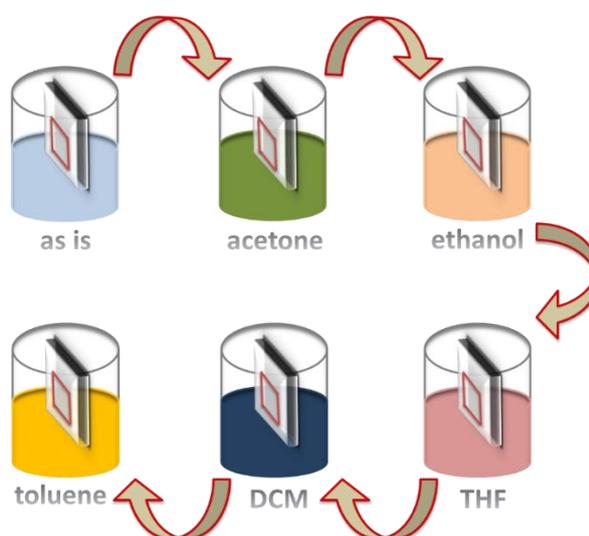
Figure 16. Schematic illustration of washing processes for PTFE transferred silicon oxide surfaces with various organic solvents

Further washing / cleaning processes were also applied with boiling water to the samples on which the square shape was scratched, to monitor the durability of the transferred PTFE features. Samples were dipped into the deionized water, heated and boiled for periods of 1 and 5 minutes, and 5 hours, respectively. (Figure 17) XPS measurements were employed in between these intervals.
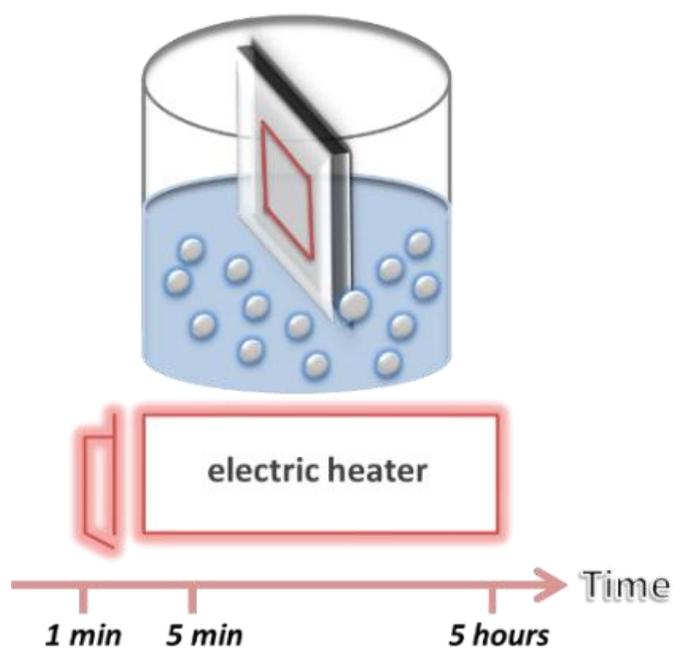
Figure 17. Schematic illustration of washing processes for PTFE transferred
silicon oxide surfaces with different amounts of time in boiling water

Chapter 3

Results and Discussion

Formation of polymer transfer films due to contacting with metal surfaces has been reported in literature extensively, and polytetrafluoroethylene was the most commonly used polymer in these studies, due to its several intriguing properties. Various reasons behind the use of polytetrafluoroethylene in tribological applications were given in the introduction part of this work. The following results will be introduced focusing mostly on analyses related to chemical and physical aspects of the polytetrafluoroethylene transfer onto counter surfaces which were contacted in sliding motion. Firstly, results of XPS measurements to monitor transferred material and its spectroscopic analysis will be given. This will be followed by experiments aimed to understand the physical aspect which refers to the estimation of minimum requirements (i.e. contact force and pressure) needed to bring about a chemical interaction between two surfaces. Then, results and discussions related to monitoring transferred patterns will be expanded with incorporation of other complementary techniques like SEM, FT-IR and AFM. In addition to these, stability of polymer transfer films and their possible applications will be given within this chapter.

3.1. XPS Studies: Monitoring Tribological Transfer onto Silicon Oxide Surfaces in a Non-Gradual Manner

XPS was used as the main characterization technique in this study, in order to analyze specimen surfaces because it is able to provide highly surface and chemical-sensitive elemental analysis, as previously mentioned. This means that we were able to obtain valuable information about chemical reactions/interactions occurring due to the contact of two surfaces, following changes in the amount of specific elements. In our case, they were silicon, oxygen, carbon and fluorine. Because PTFE consists of $-CF_2-$ groups, data to be obtained on a random point on the silicon oxide surface, within the region of C1s and/or F1s will give important clues related to chemical nature of transferred PTFE residues. Therefore, we characterized counter surfaces using three scanning modes of XPS (see Figure 11), after they were contacted with PTFE tip in sliding motion. Spectroscopic differences between slid with PTFE, and non-slid parts of counter surfaces will be used in discussions related to transfer film formation.

A few lines were drawn collaterally without using the inclined aluminum support, to implement a non-gradual PTFE transfer onto silicon oxide surface, Figure 18 shows these lines clearly on an aerial XPS spectral map created after the data was obtained in the snap-shot mode for F1s region using an X-ray spot of 30 μm - diameter and 30 μm - intervals between the data points. Then the area under each peak was fitted using the software. The x and y axes illustrate the positions of the specimen surface in the millimeter-scale, and the adjacent color bar shows the extracted area values, which means that the lighter-colored features observed within

the image belong to strong moieties that have been transferred onto the oxide surface. Transfer of polymer residues onto counter surfaces was reproducible for all the specimens prepared within two years.
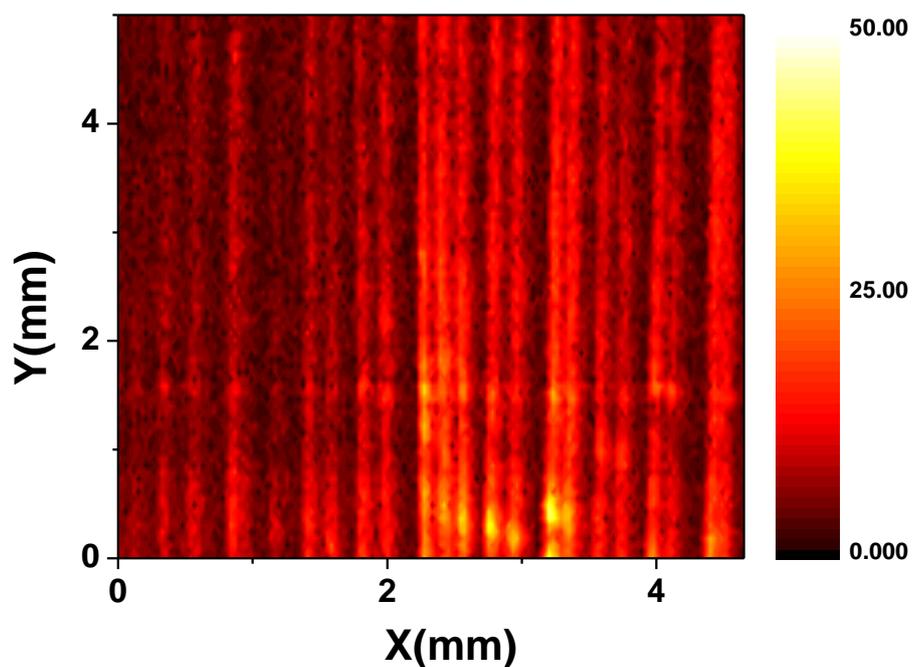
Figure 18. XPS aerial map of F1s of the specimen surface after collateral lines imparted with sliding process

Since the aerial map only does not give sufficient information, high resolution XPS spectra of F1s and C1s regions of a random point on one of the lines rubbed with PTFE were obtained, as illustrated in Figure 19. This time, aerial F1s mapping was different in the sense that fewer and longer lines were created with sliding of PTFE, though the spot size of X-ray and distances between the data points were preserved. Reproducibility of this method allowed us to control the transferred patterns and understand the type of interaction causing this material transfer.
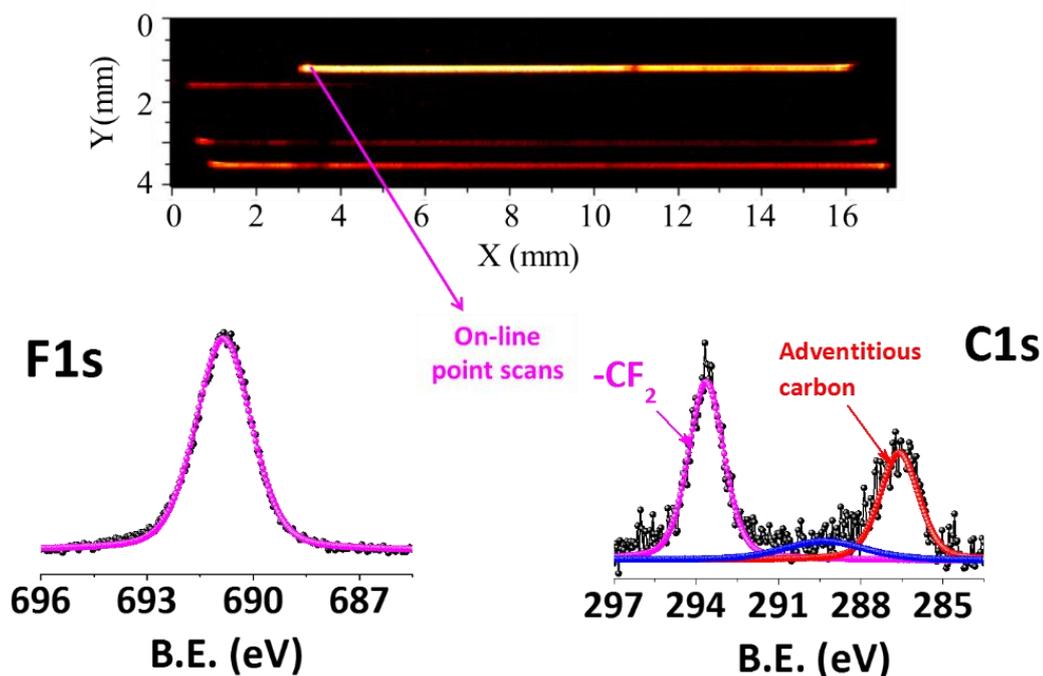
Figure 19. An aerial spectral map of the F1s peak intensity, performed on the surface of the sample where some lines were drawn by the PTFE tip. F1s and C1s regions of XPS spectra recorded on a point on the line are also shown. "Reproduced with permission from J. Chem. Phys. 141, 164702. Copyright 2014, AIP Publishing LLC."

High resolution F1s and C1s spectra explicitly reveal that the transferred species do not only contain fluorine but $-CF_2-$ groups have been transferred onto the silicon oxide surface. This finding was verified by the complementary analysis of both spectra, C1s and F1s, with respect to their positions and intensities. After the charge correction was processed, binding energy positions of C1s ($\sim$294 eV) and F1s ($\sim$691 eV) peaks were assigned to $-CF_2-$ groups of PTFE.[51] Spectra taken on a point off the scratched line did not show any F1s and the corresponding C1s peaks, but just a peak at lower binding energy ($\sim$286.5 eV) in the C1s region which is usually called adventitious carbon, and appears as hydrocarbon contamination due

to atmospheric exposure of any surface. Therefore, this peak is expected to be present in all spectra taken for specimens prepared under ambient conditions. The other reason which points to that the transferred features belong to PTFE, is the stoichiometric ratio (F:C = ~2) which was derived from the intensities of peaks. In addition to this, F1s region did not include any other secondary peak at lower binding energies, which might be an evidence of the formation of fluoride species related to metal-fluoride bonding.

As stated by Bunn and Howells in 1954, the PTFE molecule has a twisted zigzag chain with 13 carbon atoms per 180° twist and they are structured as rod-like, differently from ribbon-like hydrocarbons like polyethylene.[3], [71] (See Figure 20) In addition, smooth profile of this rod-like structure of PTFE was suggested to be providing easier slippage, resulting in easier transfer onto the counter surfaces.[3] Moreover, this material transfer between surfaces in contact, had been previously observed and reported with XPS measurements as well as with various imaging techniques.[7], [32], [72]
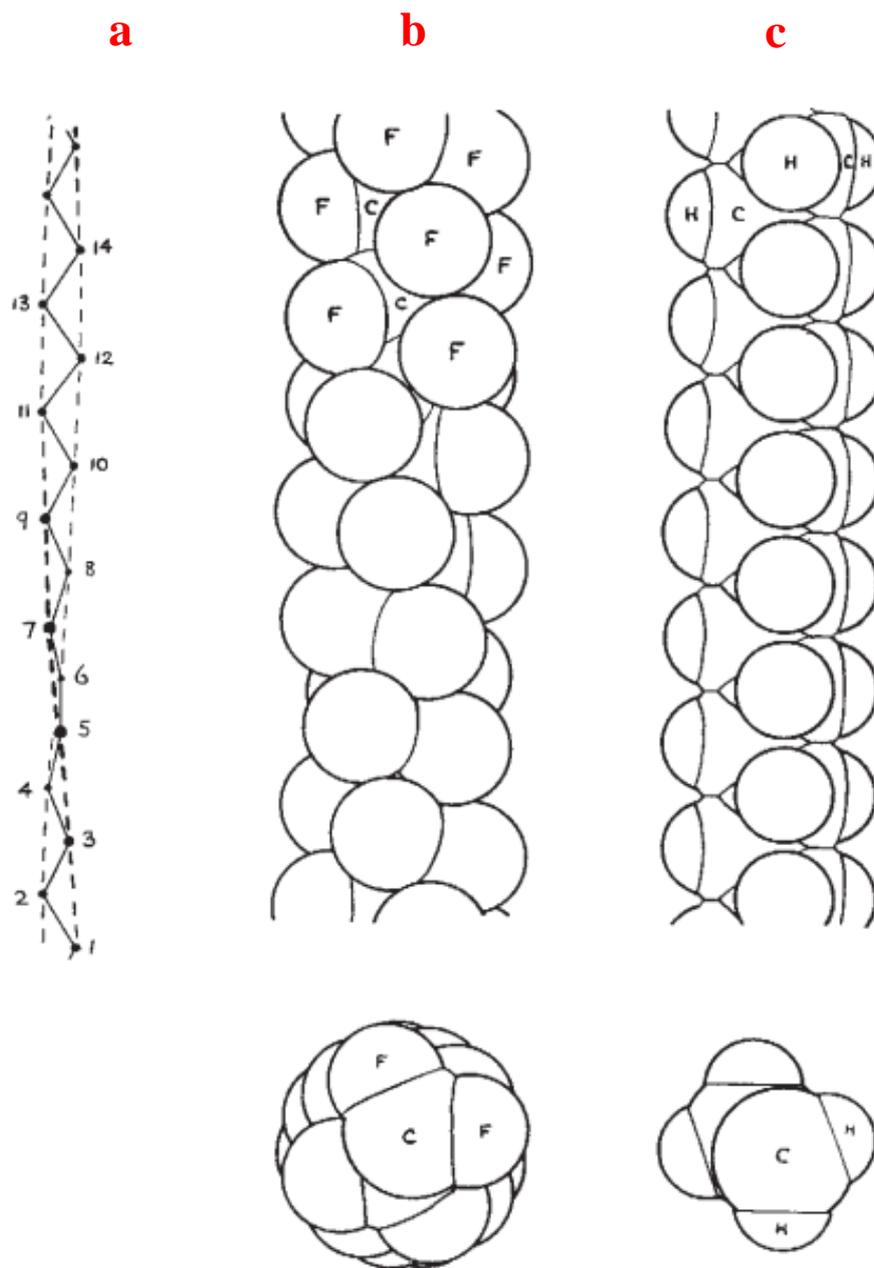
Figure 20. Differences in molecular structures of fluorocarbons (e.g. polytetrafluoroethylene) and hydrocarbons (e.g. polyethylene): a) twisted zigzag chain found in fluorocarbons b) side and end views of fluorocarbon molecule c) hydrocarbon molecule "Reprinted by permission from Macmillan Publishers Ltd: [Nature] (Bunn, C. W., and E. R. Howells. "Structures of molecules and crystals of fluorocarbons." *Nature* vol. 174 pp. 549-551 1954., copyright (1954)"

3.2. XPS Studies: Line Scan Analyses

Utilization of XPS measurements on a silicon oxide surface which was contacted with PTFE tip during sliding motion verified that copious amount of PTFE segments were transferred onto the counter surface. However, in order to elucidate the nature of this interaction in detail, we must answer two important questions about; (i) whether or not decomposition is observable on surfaces as a result of Si-F bond formation or formation of other fluorinated and chemisorbed species, and (ii) the minimum apparent contact force or pressure needed to trigger this interaction between PTFE and silicon oxide substrate.

To possibly answer these questions, inclined aluminum block was placed as a base support for silicon oxide surfaces and PTFE sliding was performed starting from a position where the tip was not touching the counter surface. While the tip is moved towards this inclined silicon oxide surface using this setup, there will be a point where PTFE tip touches, interaction begins and transfer occurs. In this way, experiments where a gradual tribological transfer of PTFE onto counter surface occurs, have been conducted. In an aerial map of the F1s peak which was recorded in the snapshot mode using an X-ray spot diameter of 30 μm and intervals of 30 μm between the data points, a gradual increase in the intensity of the F1s peak can be observed along the imparted lines, as well as features which can be attributed to "stick-slip" motion of the tip. (See Figure 21)
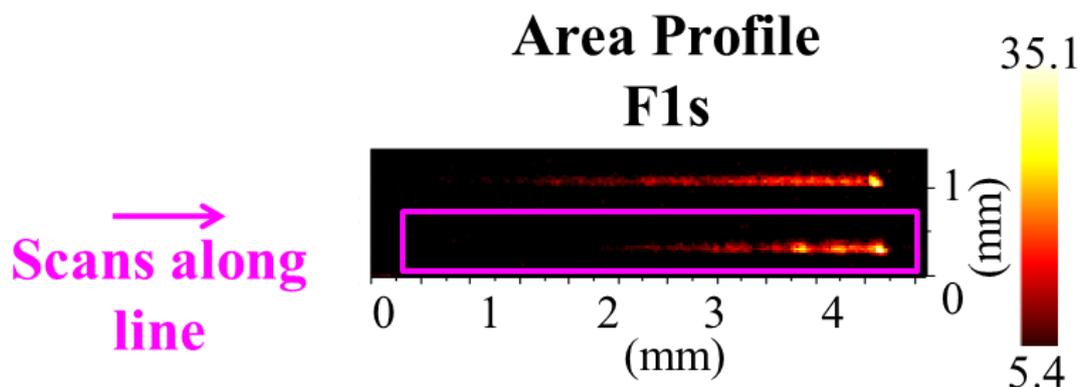
Figure 21. An aerial spectral map of the F1s peak intensity illustrating gradual increase of PTFE transfer on the surface of the specimen. "Reproduced with permission from J. Chem. Phys. 141, 164702. Copyright 2014, AIP Publishing LLC."
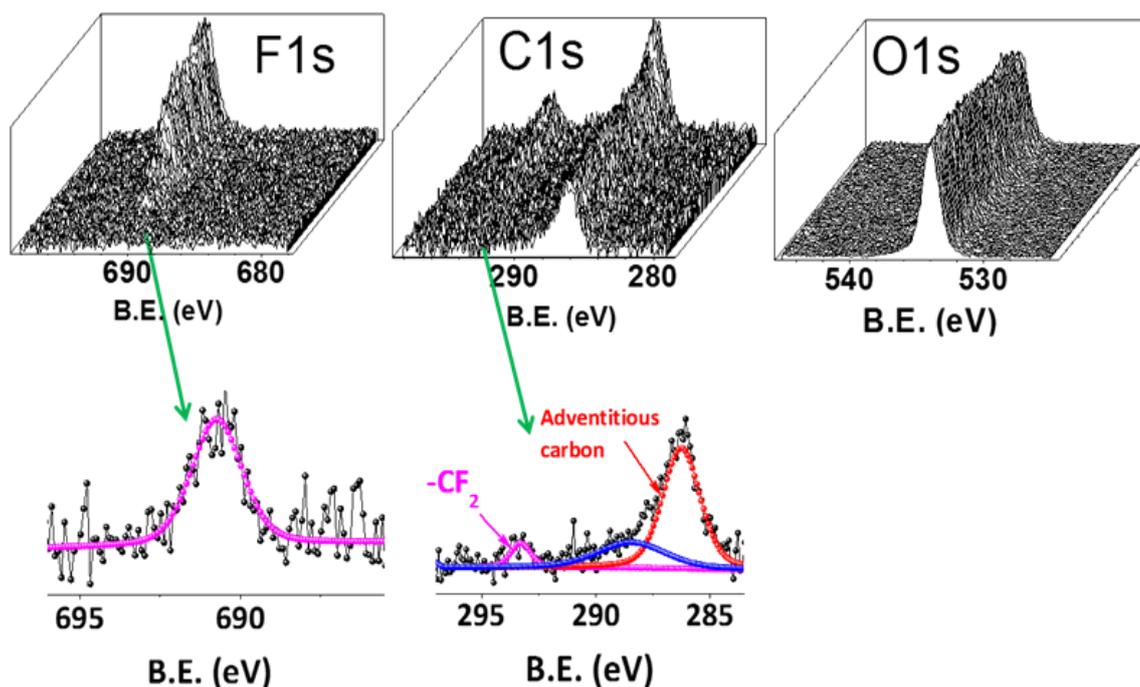
Figure 22. Recorded line scan spectra of F1s, C1s, and O1s regions. The spectra at the onset are also shown for the F1s and C1s regions below. "Reproduced with permission from J. Chem. Phys. 141, 164702. Copyright 2014, AIP Publishing LLC."

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Line scan analyses for F1s, C1s and O1s regions were performed along the line, as illustrated with magenta frame in Figure 21. Obtained spectra of line scans for F1s, C1s and O1s regions using X-ray spot size and step sizes of 70 μm, are shown in Figure 22, where a gradual increase in intensities of F1s and C1s is observed, while a consistent decrease in O1s peak belonging to the oxide layer of the substrate, takes place. All of these findings point to the fact that the PTFE is faithfully transferred onto the counter silicon oxide surfaces.

Furthermore, a linear increase of PTFE transfer was clearly observed with addition of the plot illustrating the area of fitted peaks for F1s, C1s and O1s regions with respect to steps which are extracted from data points taken on the designated line. (See Figure 23) The onset position shown in the plot, was identified with respect to peak area of C1s which is below the computed noise level. Moreover the identified onset point on C1s, is well-correlated with the increase in F1s as well as a decrease in O1s. It is also worth to point out that no other peak was observed in F1s region related to metal-fluoride or oxide-fluoride bonding although this region is highly sensitive for fluorinated species that might appear with possible decompositions. In addition to this, transfer of PTFE even at the slight touch is also verified, as illustrated in high resolution spectra derived from line scans in Figure 22. This finding is similar to what was reported in an experiment, where PTFE had been transferred to counter tungsten surface on a simple contact, probably through an organometallic reaction.[3], [73]
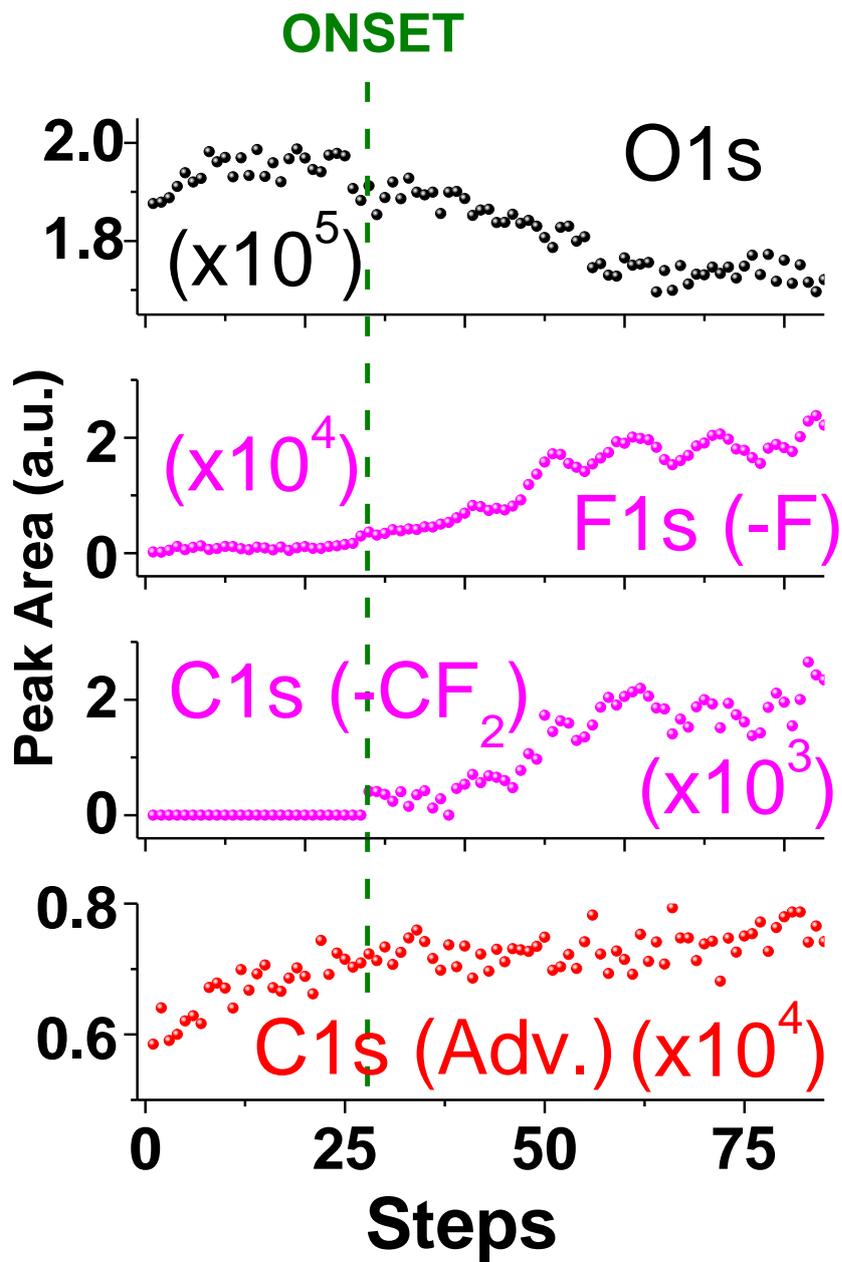
Figure 23. Plot displays peak areas of F1s, C1s and O1s regions, along the scanned line, from which the onset of the PTFE transfer is evaluated. "Reproduced with permission from J. Chem. Phys. 141, 164702. Copyright 2014, AIP Publishing LLC."

3.3. Estimation of Minimum Apparent Contact Force and Pressure Enabling Tribological Transfer

Considering all of these issues and procedures explained in the experimental chapter (See section 2.3.3.), a maximum contact force of 0.06 mN was calculated to occur at the onset using the measured parameters and the standard elastic beam deflection formula. During the sliding, the amount of deflection observed on the tip was very small (maximum 50 μm for a line of PTFE scratch length of 5 mm) and a deflection rate of about 10 μm/s suggested us to ignore viscoelastic and thermal effects that might appear.

To calculate the pressure arising between the surfaces, the apparent contact area was taken into account using the SEM images of the tip which is given in Figure 13, with approximate dimensions of 100 μm × 125 μm. We identify this area as apparent due mainly to the multi-asperity character of the PTFE tip, in complying with the common usage in previous studies.[74], [75] Using the value of apparent contact area, a maximum apparent contact pressure arising at the onset, where tribological transfer of PTFE started, was calculated to be 5 kPa. This value is significantly lower than contact pressures reported varying from 6 to 40 MPa in studies where atomic force microscopy and tribometer-based measurements were utilized.[74]–[77]

3.4. SEM Imaging of Transferred Patterns

To image morphological changes caused by PTFE transfer onto the silicon oxide surfaces, we utilized SEM on two different specimens. In the first sample, PTFE tip was slid as a single line, not as a certain shape or collateral horizontal lines. The SEM images provided complementary results supporting our XPS findings that stable PTFE segments were imparted onto the counter silicon oxide surfaces. Figure 24 shows the scratched PTFE line in two segments, one of which is a zoomed version of other. Accordingly, the line has a length of ~5 mm and a thickness of ~100 µm using optical and SEM images of PTFE tip which were given in Figure 13. However, this is understandable in account of the multi-asperity character of PTFE tip that might have caused interlacing of the individual lines.
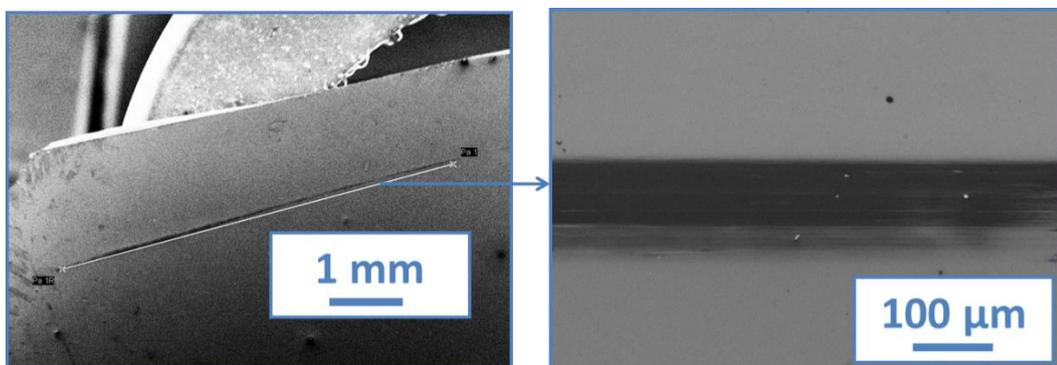
Figure 24. Changes on the surface morphology upon a single line-PTFE transfer demonstrated by SEM. "Reproduced with permission from J. Chem. Phys. 141, 164702. Copyright 2014, AIP Publishing LLC."
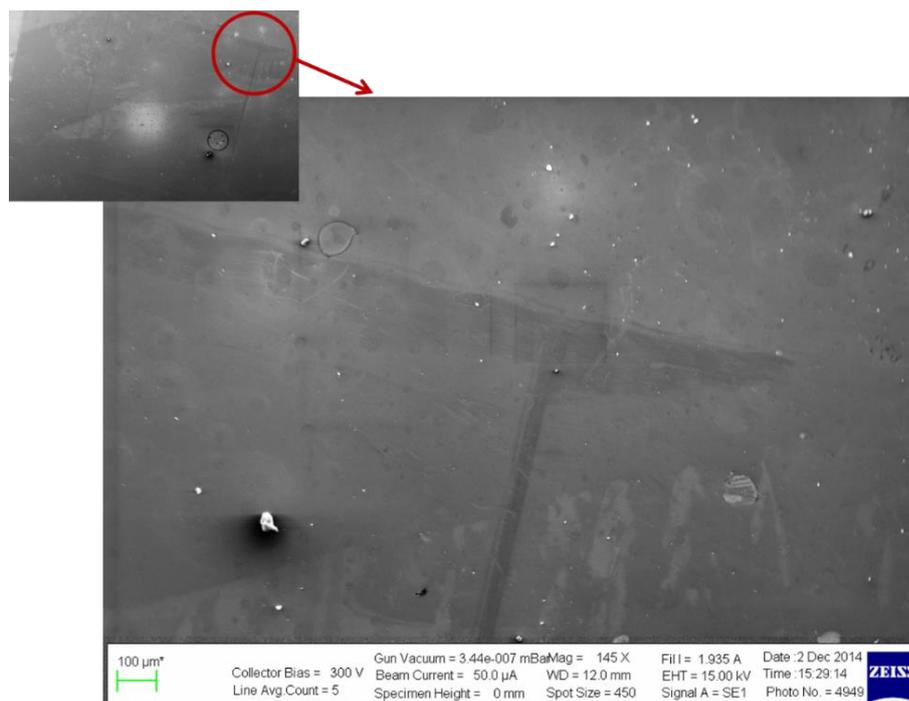
Figure 25. SEM image of the changes on the surface morphology upon a square shape-PTFE transfer

Secondly, SEM analyses were performed on a silicon oxide sample on which PTFE pattern of a square-shape was transferred onto its surface, which was also used for chemical and time-dependent-durability tests. The edge of the square-shape pattern is observable as shown in Figure 25, in addition to several morphological defects on the surface. These arise as a result of the differences in contrast, which might be due to formation of residues after cleaning of the specimen with various organic solvents. It is also possible that structure of the pattern was deformed during durability tests performed under ambient conditions. Edges of the patterned square have thickness varying between 50 μm and 150 μm which is consistent with previously mentioned statement related to multi-asperity character of the PTFE tip.

3.5. FT-IR Results

FT-IR measurements were performed on two PTFE transferred silicon oxide samples, first of which was hand held, and the other was slid using the x-y stage. The surfaces have several horizontally imparted PTFE lines. After subtracting the background measurement which was performed on a blank, non-scratched silicon oxide surface, spectra obtained are illustrated in Figure 26. Both spectra exhibit typical PTFE peaks[78], as highlighted with yellow stars, verifying that PTFE transferred onto the counter silicon oxide surface faithfully. Moreover, intensity of the peaks for the specimen on which the PTFE was slid by hand was observed to be higher than the other sample. These differences in the IR intensity of the peaks confirms that PTFE density transferred onto counter surfaces, can be increased by larger applied contact pressure. However, obtaining quantitative information about the amount of PTFE segments from these spectra seems is difficult due to the very low quantity of the transfer.
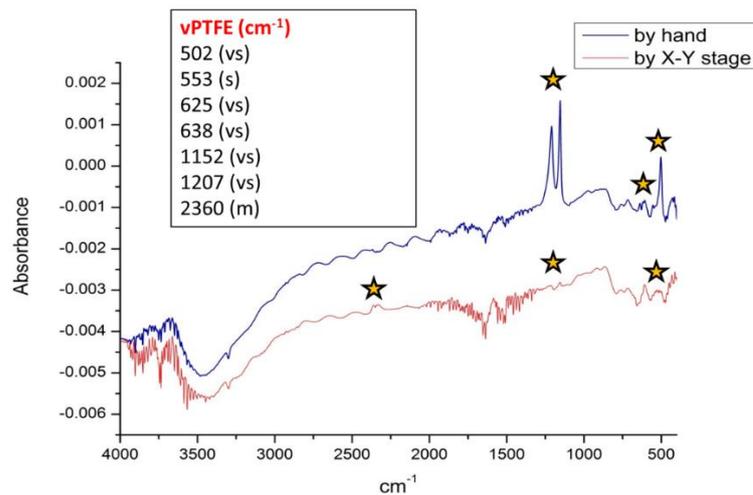
Figure 26. FT-IR absorption spectra of silicon oxide substrate on which PTFE tip was slid by "hand-roughly" (blue) and "x-y stage-temperately" (red)

3.6. AFM Results

AFM measurements were performed for topographical analysis of specimen surface as a complementary technique to SEM. Contact mode was utilized using silicon cantilevers, on a silicon oxide surface before and after PTFE transfer consisting of several collateral, horizontal lines that were imparted. Figure 27 illustrates a 3-D representation of the topographical maps obtained before and after the transfer, which clearly reveal significant differences appearing on the surface morphology. While the 20 μm x 20 μm areal map obtained before PTFE transfer has an average surface roughness of about 0.75 nm, this value increased to 6 nm within a 40 μm x 40 µm areal map obtained after the transfer. As mentioned in several studies[43], [74], the alignment of PTFE lines is observed to be along the sliding direction in our work. Furthermore, observation of several lines in a 40 μm - axis length verifies our justification about the multi-asperity character of tip once again. The outcome of these studies is that PTFE lines can be transferred in sub-micron level using specialized tips, consistent with our findings reported earlier in this thesis.
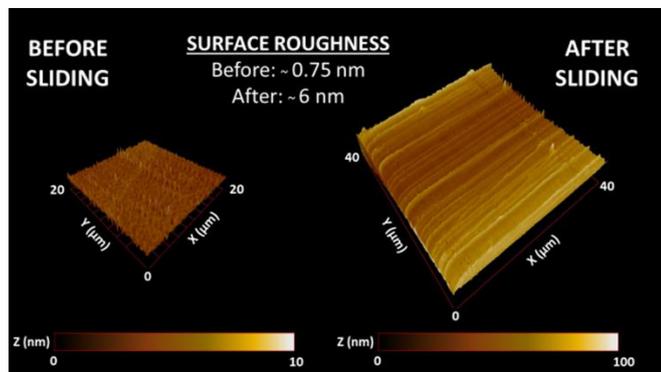
Figure 27. 3-D representation of AFM topographical map of silicon oxide surface before and after PTFE sliding

3.7. Enhancement of Hydrophobicity as an Application

Due to low surface energy characteristics, various surfaces coated with PTFE have been reported to exhibit low wettability (hydrophobicity) as mentioned within previous chapters. Although these films are realized with different coating methods (e.g. chemical vapor deposition[46], radio frequency-magnetron sputtering deposition[47], spray-and-dry method[48]), there is no wettability study related to tribologically-transferred PTFE films. Because a simple transfer of polymeric features onto the counter surface is possible with slight touches of the tip, we envisioned to control and tune the wettability characteristics of surfaces, which is of potential significance as an application, as illustrated in Figure 28.
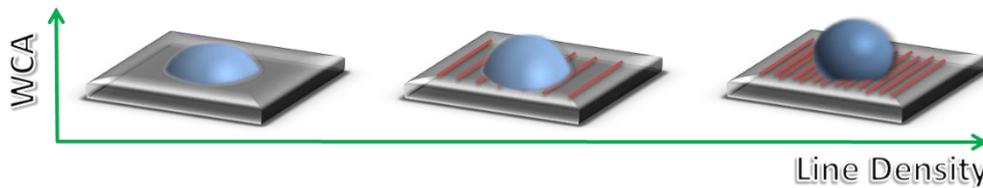
Figure 28. Schematic illustration of the rise in water contact angle with respect to increasing line density of PTFE

In accordance with this purpose, several specimens were prepared with sliding PTFE tip with various number of lines per area, resulting in transfer of PTFE onto the counter silicon oxide surfaces with different densities. As a notation in this study, line density meaning the number of lines per 1 mm is used. For example, lines drawn with 100 μm intervals correspond to a line density of 10 lines/mm.

Figure 29 shows the water contact angle (WCA) measurements which were carried out after the mentioned features were transferred. As can be seen from the figure, there is a clear tendency of increasing contact angles with respect to the increase in the line density. While a blank, non-coated silicon oxide surface has a WCA value of about 40^0, a WCA value above 100^0 was obtained when 40 lines per mm were transferred, which is the highest applied line density due to the limitation of our x-y stage. Increase in hydrophobicity was also observed by the images of droplets recorded by an optical microscope, as also depicted in the same figure.
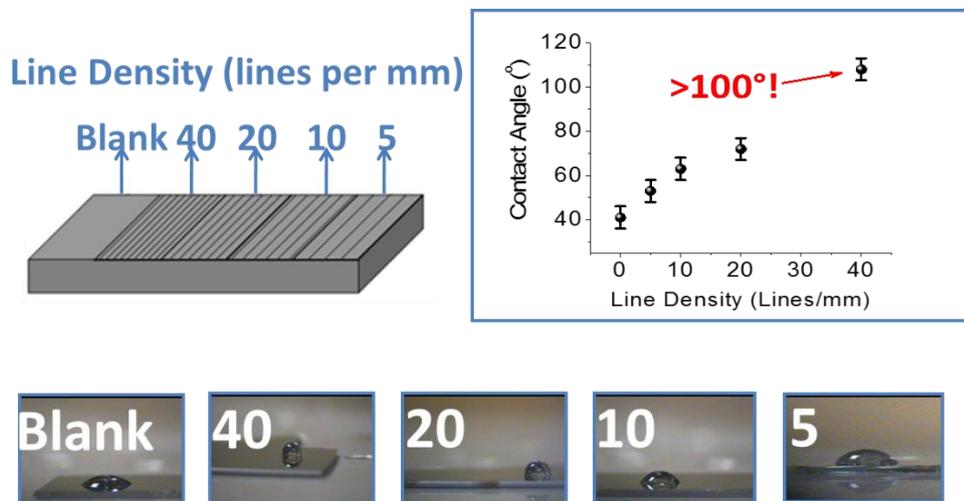
Figure 29. Water contact angle measurement results for the surfaces with various PTFE line densities. Images of droplets taken by the optical microscope are also presented. "Reproduced with permission from J. Chem. Phys. 141, 164702. Copyright 2014, AIP Publishing LLC."

The reason leading to a significant increase in WCA values was probably not only due to altering the surface energy of silicon oxide surfaces, but morphological changes created with the transferred patterns were also effective on this improvement, as the significance of surface texturing was emphasized on wettability characteristics before.[79]

3.8. Durability of Transferred PTFE Patterns with Time

Over the last 2 years, we have prepared many samples on which PTFE lines were faithfully transferred as verified by XPS measurements. Some of these specimens were characterized after certain times and it was confirmed that transferred PTFE patterns on these silicon oxide surfaces were stable with respect to F1s and C1s spectra. As illustrated in Figure 30, comparison of intensities obtained in F1s areal spectral maps, utilized by using an X-ray spot size of 400 µm and step size of 400 µm between data points, on the same specimen after 3 months and 7 months, justifies our statement that we are able to create stable (7 months at least) polymeric features via tribological transfer. Acetone washing processes applied before XPS measurements show that the features are also durable against chemicals, and not just only time.
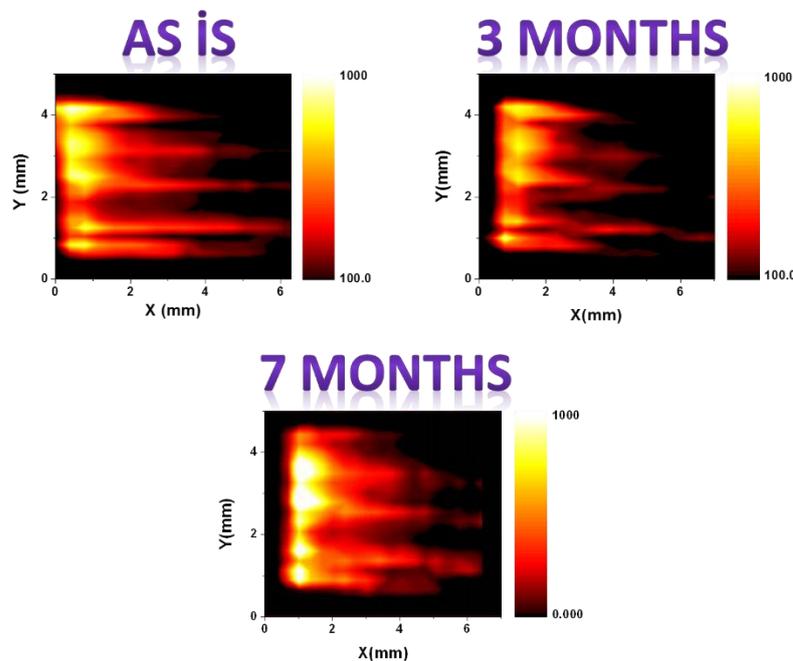
Figure 30. Time-dependent-durability representation of PTFE transferred specimens with F1s areal spectral maps performed with different time intervals

3.9. Implementation of Cleaning Processes with Organic Solvents

After the stability of PTFE-transferred samples against time and acetone was verified utilizing XPS measurements, we prepared and systematically analyzed durability of specimens against various chemical and physical treatments. Figure 31 displays the 3-D representation of F1s areal maps which were recorded after flashing the sample with flowing nitrogen gas, washing with ethanol and acetone in ultrasonic bath for 15 minutes, in sequence. No significant decrease in F1s intensity was observed, verifying the fact that transferred PTFE features were stable even after all these chemical treatments.
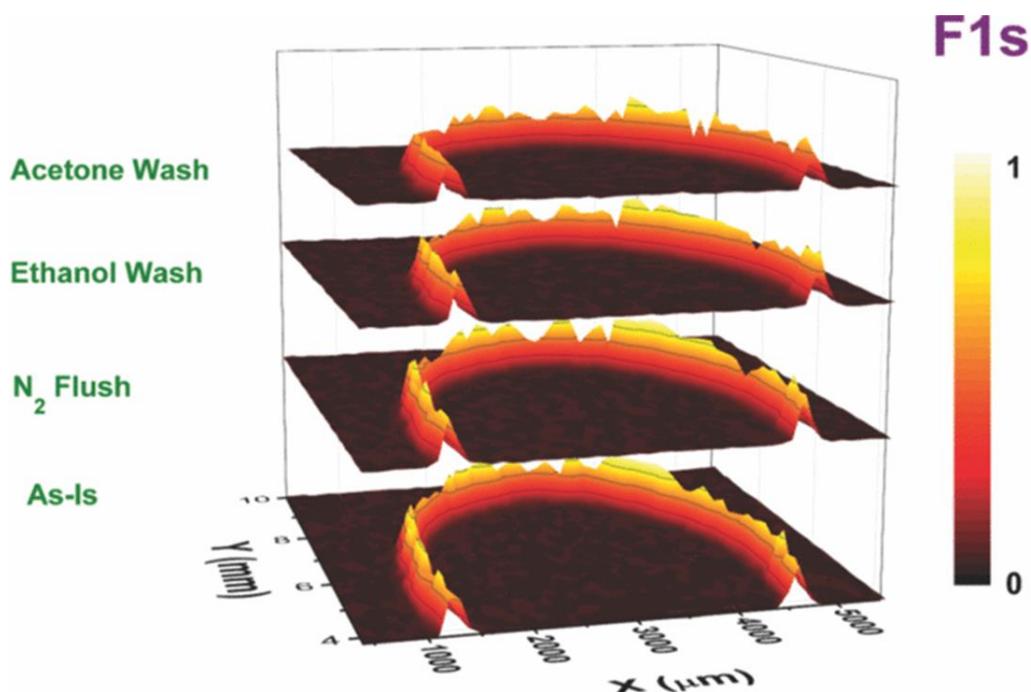
Figure 31. F1s areal maps of a section of a circular scratch drawn, recorded after several physical and chemical washing steps. "Reproduced with permission from J. Chem. Phys. 141, 164702. Copyright 2014, AIP Publishing LLC."
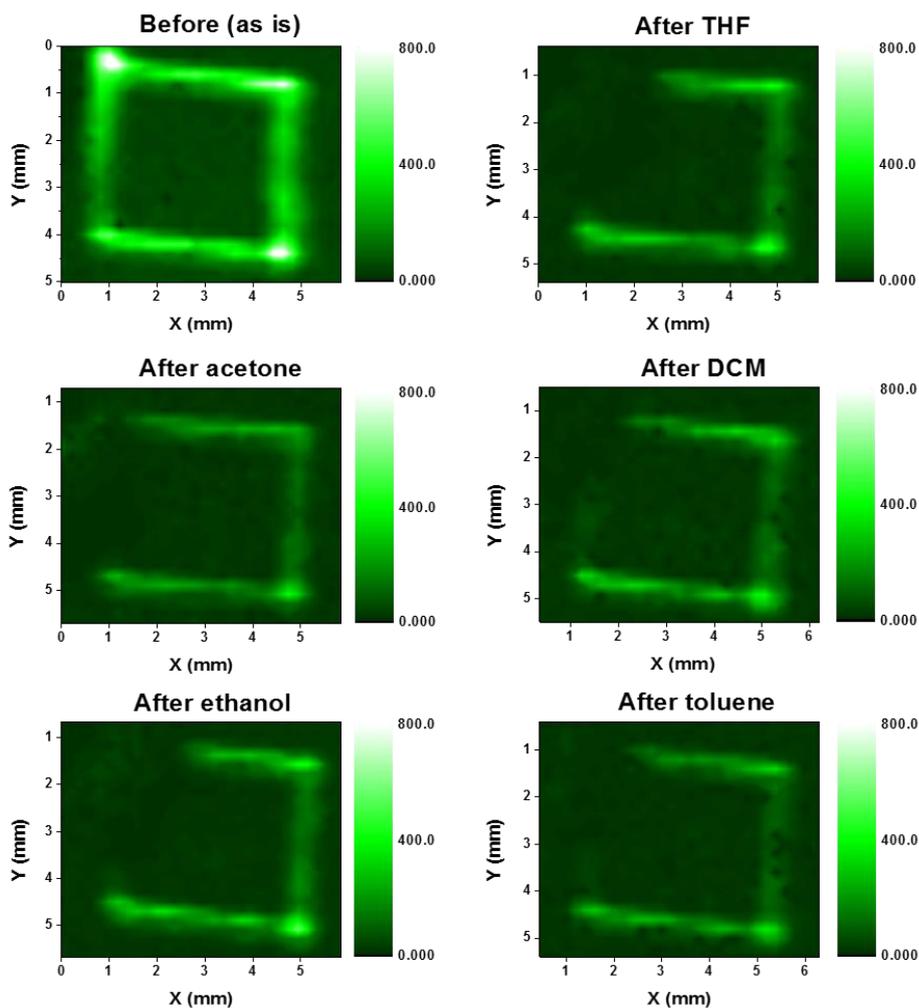
Figure 32. F1s areal maps of a square shaped-PTFE pattern transferred onto silicon oxide surface after consecutive chemical washing steps using several organic solvents.

Then, our investigation was extended with addition of washing processes using various organic solvents like acetone, ethanol, THF, DCM and toluene. After all treatments applied in order, XPS analyses were conducted. As shown in Figure 32, the imparted PTFE feature was observable after all these chemical washing steps, though there is some change in the F1s intensity. All of these findings point to the fact that the nature of the interaction at the polymer-metal interface was indeed chemical.

3.10.   Implementation of Cleaning Processes with Boiling Water

In a private communication made with Christopher P. Junk from DuPont Central Research and Development, it was suggested to use boiling water treatment to the PTFE-transferred silicon oxide specimens, in addition to the chemical washing processes performed, to possibly give further evidence about the nature of this interaction. Thus, samples on which square PTFE patterns were imparted, were dipped into boiling water for 1 and, 5 minutes, and 5 hours in that order. Areal maps recorded on these time intervals did not show a significant decrease in F1s intensity, even after dipping in boiling water for 5 hours, strongly supporting the fact the nature of this interaction is chemical. (See Figure 33)
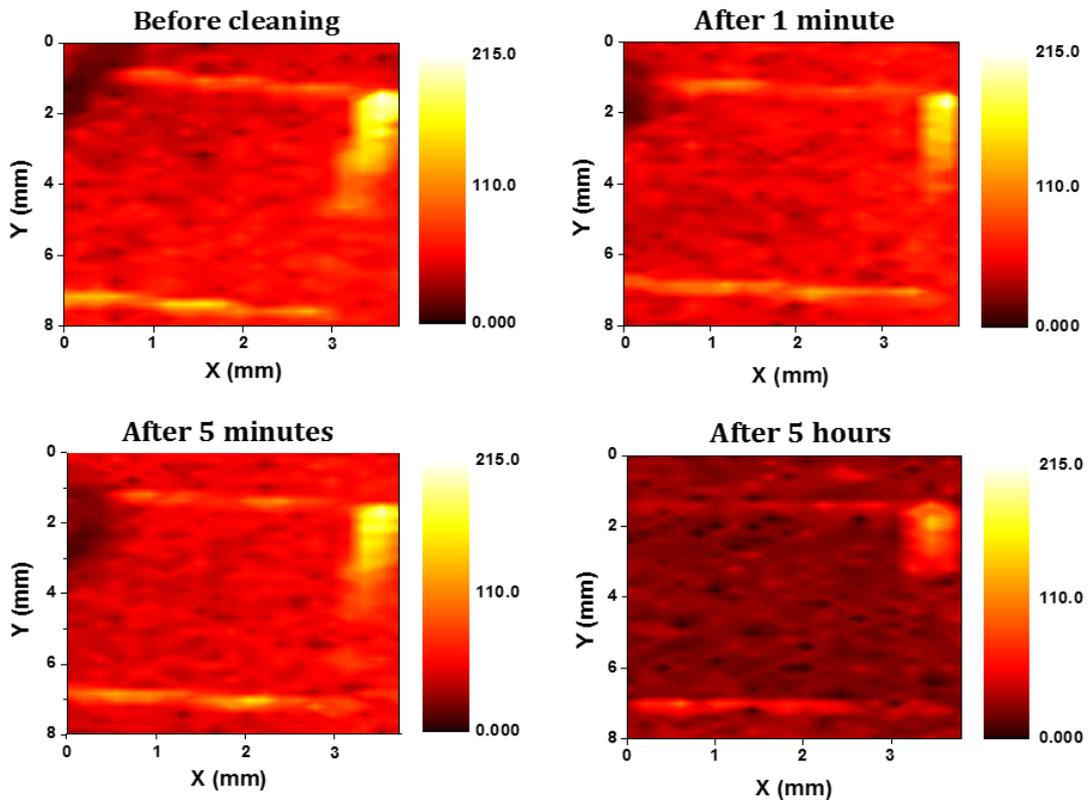
Figure 33. F1s areal maps of a square shaped-PTFE pattern transferred onto silicon oxide dipped into boiling water for various periods of time

3.11. Monitoring Controlled Transfer of PTFE Patterns onto Silicon Oxide Surfaces

Ability of controlling PTFE patterns transferred onto the counter surface via our tribological method was previously emphasized. Figure 34 presents F1s areal map which was obtained in the snapshot mode with X-ray spot size of 50μm and steps of 50μm between data points, from a silicon oxide surface onto which PTFE was tribologically transferred in the pattern "bil uni" (the abbreviation of Bilkent University). Appearance of the pattern reveals that tribological transfer is successfully controllable at the micrometer-level which is the highest imaging resolution within the capability of our XPS instrument. This finding might lead to a future study that might focus on controlling such transfers in the nanometer-scale.
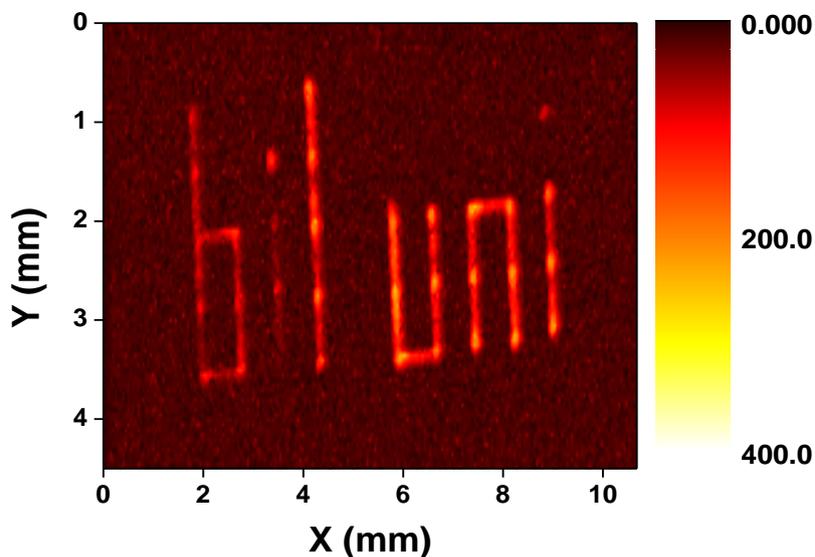
Figure 34. F1s areal map of a silicon oxide surface, onto which PTFE was tribologically transferred in the pattern "bil uni" (the abbreviation of Bilkent University). "Reproduced with permission from J. Chem. Phys. 141, 164702. Copyright 2014, AIP Publishing LLC."

3.12. XPS Studies: Monitoring Tribological Transfer onto Polymer Surfaces

Although literature is rich with studies focused on tribological interaction arising between polymer and metal surfaces in contact, there are not many examples dealing with the chemical nature of polymer-polymer interfaces. One of these rare studies was reported by Baytekin *et al.* relating the material transfer with differences in elasticity between contacted materials. According to the criterion which was developed by them, stiffness of the contacting materials should be different with respect to each other, for material transfer to occur between these surfaces.[38] In addition, there are also studies which have mainly focused on the mechanism of friction and adhesion which takes place between two sliding polymer surfaces. According to two leading studies where sliding experiments were realized on polystyrene and poly(vinylbenzyl chloride) (PVBC) surfaces, some significant findings which were reported by Israelachvili et al., can be summarized as follows; (i) obtained friction forces are definitely related with adhesion hysteresis (ii) cross-linking of the polymer surfaces reduce the adhesion (iii) increase in the number of chain ends at polymer surfaces, resulting from either scission of chains or addition of short chain polymers, also increases the adhesion and friction, and (iv) continuous changing in sliding mechanisms take place due to easy-shearing characteristics of polymers; thus steady-state conditions are not valid in polymer-on-polymer sliding.[80], [81]

In order to contribute to the understanding of the nature of interactions between contacting surfaces, we have also prepared polymer surfaces, and conducted sliding experiments using the same experimental setup with the PTFE tip. As was also mentioned in the experimental part (See section 2.3.1.), PS, PVC and PMMA were spin-coated from their respective solutions, onto the thermally oxidized silicon surfaces. Results of the XPS measurements utilized to monitor and spectroscopically analyze transferred patterns are given below.

3.12.1. Polystyrene Coated Surfaces

Figure 35 illustrates the results obtained from XPS measurements performed on PS-coated and then PTFE slid - silicon oxide surfaces. As can be seen in Figure 35a, individual lines scratched collaterally on PS-coated surface are clearly observable in the F1s areal mapping. This F1s spectral map was utilized using X-ray spot size of 50 μm and step size of 50 μm between data points. Similar to non-coated silicon oxide surfaces, lighter-colored features were observed again within the image and these can be stated to belong to PTFE moieties that have been faithfully transferred onto the PS-coated oxide surface. In order to justify this statement, high resolution spectra were also taken for F1s and C1s regions, at random points on and off one of these lines, as shown in Figure 35c and 35d, respectively. Because polymer coated surfaces are considered as insulators, flood gun was used for the charge compensation and then peak positions were corrected with respect to the C1s peak arising from atmospheric hydrocarbon contamination which should be observed at 285.00 eV. After this charge correction was processed, binding energy positions of C1s (~292.5 eV) and F1s (~689.6 eV) peaks which

were observed on on-the-line spectra, were assigned to the -CF$_2$ groups similar to the sliding of PTFE on non-coated silicon oxide surfaces. Spectra taken on a point off the scratched line did not include F1s and C1s peaks and this satisfies our expectation that PTFE was also transferred onto counter PS coated oxide surfaces. We would also like to point out that a third peak (~291.4 eV) observed within C1s spectra which were obtained from both on and off the scratched line scans, belongs to the shake-up satellite of polystyrene polymer.[51]

Figure 35. (a) F1s areal map of a polystyrene-coated silicon oxide surface which was slid with PTFE. (b) Chemical structure of polystyrene. Also the spectra taken on (blue) and off (orange) a point placed one of the lines are shown for the (c) F1s and (d) C1s regions.

3.12.2. PVC Coated Surfaces

After PTFE transfer onto PS-coated oxide surfaces was verified, we also utilized XPS measurements on PVC and PMMA-coated specimens. Figure 36 shows the results obtained from these measurements performed on spin-coated with PVC and then slid with PTFE, silicon oxide surfaces. As can be seen in Figure 36b and 36c, a similar behavior was observed in transfer of PTFE onto PVC coated surfaces, as compared to previously mentioned counter surfaces. Individual lines which were scratched collaterally on PVC surface using the same experimental technique as mentioned previously, are observable in the F1s areal mapping which were obtained using X-ray spot size of 50 μm and step size of 50 μm between data points.

In order to understand the chemical nature of these residues, high resolution spectra were taken on a random point on the specimen surface, for the F1s and C1s regions, as shown in Figure 36c and 36d, respectively. Binding energy positions of the peaks were corrected with respect to the position (285.90 eV) of the carbon atom in the CH_2 group of PVC. (See Figure 36b) After this charge correction, it was observed that on-the-line C1s region was consisting of three respective peaks which has been arisen at 285.90, ~287.30 and ~292.85 eV, while F1s region introduced just one peak at 689.80 eV. However, the peaks at ~292.85 eV and 689.80 eV were not observed within the spectra taken on a point off the scratched line, which verifies PTFE transfer onto counter PVC coated oxide surfaces. Slight differences in the peak positions within both C1s and F1s regions, as compared to results obtained from non-coated and PS-coated specimens, were mainly attributed to the

different charging processes. This is consistent with the previously mentioned phenomena in polymer-on-polymer tribology, which is continuously changing sliding mechanisms and non-steady-state conditions due to complex wear characteristics of polymers.[80]
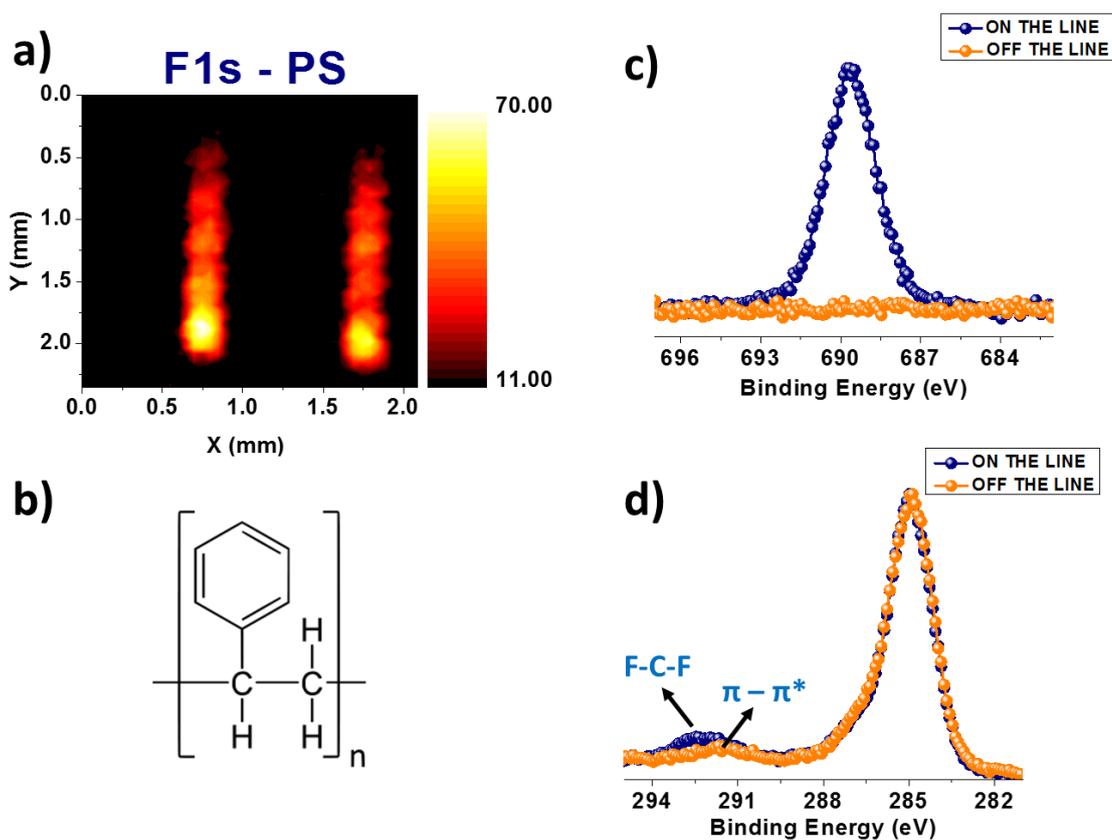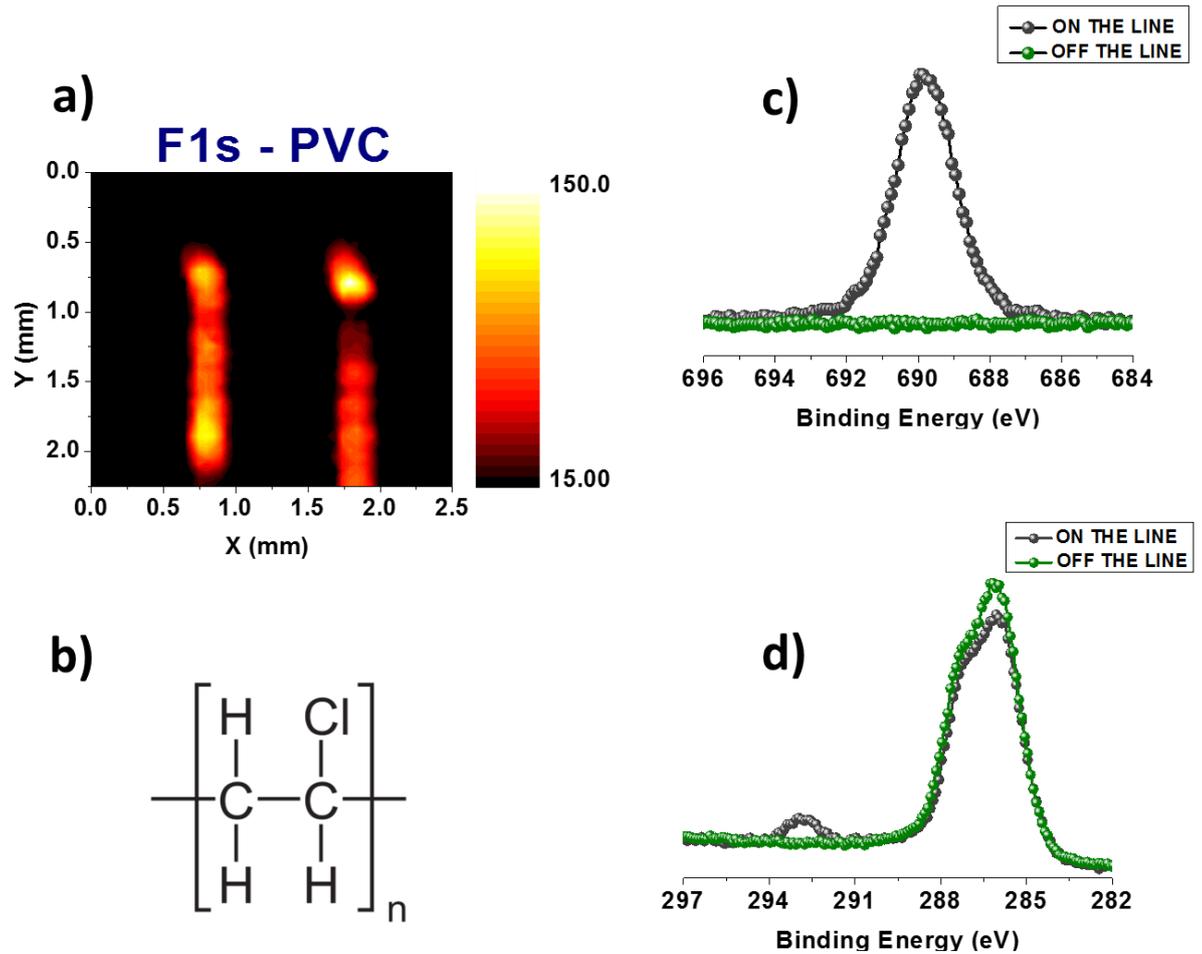

Figure 36. (a) F1s areal map of a polyvinylchloride-coated silicon oxide surface which was slid with PTFE. (b) Chemical structure of polyvinylchloride. Also the spectra taken on (grey) and off (green) a point placed one of the lines are shown for the (c) F1s and (d) C1s regions.

3.12.3. PMMA Coated Surfaces

Results of XPS measurements obtained on PMMA-coated oxide surfaces which were tribologically interacted with PTFE, show similarities with observations on PS and PVC-coated specimens. For also this specimen, transferred material residues in the shape of individual lines were observed in F1s areal spectral mapping which were obtained using X-ray spot size of 50 μm and step size of 50 μm between data points.(See Figure 37b) High resolution spectra within F1s, C1s and O1s regions, were taken on and off a point placed one of the lines on the specimen surface and they are given in Figure 37c, 37d and 37e, respectively. After the charge correction was made with respect to hydrocarbon contamination at 285.00 eV, four peaks which were observed within off-the-line C1s region (285.00, ~285.80, ~286.90 and ~289.30 eV) were attributed to CH_2, -C-, $O-CH_3$ and O=C groups.[51] (See Figure 37a and 37d) However, an additional peak at ~292.70 eV was observed in the spectrum taken on the scratched line and positions of these peaks which has arisen within the on-the-line C1s and F1s regions, give valuable information about the verification of PTFE transfer onto the counter surface. Finally, O1s spectrum consists of two peaks at 532.40 eV and 534.00 eV, which belong to two different oxygen atoms (O=C and C–O–C) in the structure of PMMA.
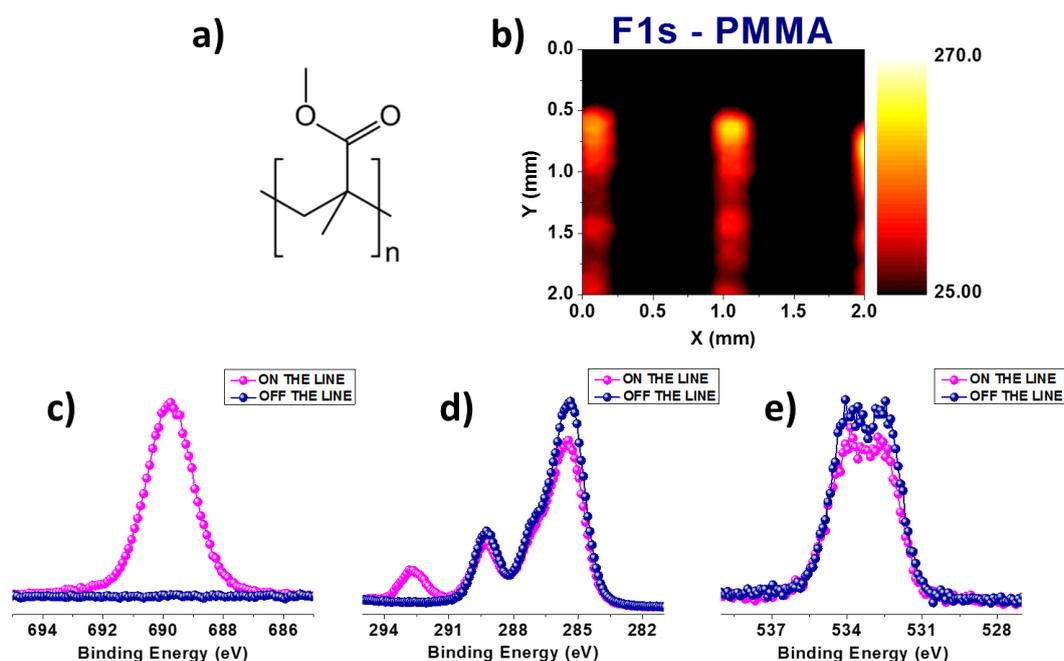
Figure 37. (a) Chemical structure of poly(methyl methacrylate). (b) F1s areal map of a poly(methyl methacrylate)-coated silicon oxide surface which was slid with PTFE. Also the spectra taken on (magenta) and off (blue) a point placed one of the lines are shown for the (c) F1s (d) C1s and (e) O1s regions.

For all three different polymers that were coated on silicon oxide surfaces and then interacted with PTFE, material transfer from PTFE to these surfaces was verified using the chemical sensitivity of XPS, even if peaks were observed at different positions due to charging issues or changing transfer mechanisms. The direction of this material transfer, which takes place from PTFE to other polymer surfaces, can be attributed to the relative stiffness criterion of Baytekin *et al.* considering large differences in their modulus of elasticity (PTFE: 0.55 GPa, PS: 3.93 GPa, PVC: 1.54 GPa and PMMA: 3.52 GPa).[38]

Chapter 5

Conclusion

In this thesis, PTFE was transferred onto counter thermally-oxidized silicon as well as PS, PVC and PMMA-coated surfaces using a simple tribological transfer method, and the physical / chemical nature of this transfer was investigated using various characterization techniques like XPS, SEM, AFM, FT-IR as well as WCA measurements.

Preparation of non-coated and coated silicon oxide surfaces was introduced. Then, detailed explanation and utilization of tribological transfer method in both gradual and non-gradual manner in order to form desired PTFE patterns on these surfaces, as well as procedures of washing / cleaning steps applied to analyze the stability of transferred material were included. After prepared specimens were contacted and slid with a PTFE tip using a special rig, XPS results revealed that PTFE was faithfully transferred onto these silicon oxide and polymer surfaces upon even the slightest contact. While SEM and AFM techniques were utilized to verify that some stable morphological changes could be observed on silicon oxide surfaces upon this PTFE transfer, infrared spectroscopy demonstrated the presence of PTFE molecules.

In order to estimate the contact force and pressure which is required to initiate this material transfer, detailed characterizations were carried out on specimens on which PTFE amount was gradually increased along the sliding direction. This was achieved with the use of inclined supports while the sliding was

taking place. This gradual increase was related with the increasing contact force and resulting deflection of the PTFE tip, using the elastic beam deflection formula. Estimated values of contact force and pressure were 0.06 mN and 5 kPa, respectively and they were lower by two orders of magnitude than previously reported values in literature.

Significant durability of transferred PTFE patterns against time, various organic solvents and boiling water was verified following the changes in intensities of specific elements within XPS spectra. The results showed that the interactions arising at polymer and semiconductor interfaces during the sliding have most likely taken place with the formation of chemical bonds.

Contact angle measurements obtained on silicon oxide surfaces revealed that there was a clear tendency of increasing contact angles with respect to the increase in the amount of transferred PTFE. Hence, the simple transfer method described within the context of this thesis used to study the tribological interaction of PTFE with silicon oxide and various polymer surfaces would provide a new point of view with regards to tuning the wetting characteristics of surfaces for numerous potential applications.

References

[1]   D. Tabor, "Tribology—the last 25 years A personal view," *Tribol. Int.*, vol. 28, no. 1, pp. 7–10, 1995.

[2]   H. P. Jost, *Lubrication: Tribology; Education and Research; Report on the Present Position and Industry's Needs (submitted to the Department of Education and Science by the Lubrication Engineering and Research) Working Group*. HM Stationery Office, 1966.

[3]   B. Bhushan, *Introduction to tribology*. John Wiley & Sons, 2013.

[4]   D. Dowson, *History of Tribology. 2nd*. London: Professional Engineering, 1998.

[5]   S. Bahadur, "The development of transfer layers and their role in polymer tribology," *Wear*, vol. 245, no. 1, pp. 92–99, 2000.

[6]   E. L. Yang, J.-P. Hirvonen, and R. O. Toivanen, "Effect of temperature on the transfer film formation in sliding contact of PTFE with stainless steel," *Wear*, vol. 146, no. 2, pp. 367–376, 1991.

[7]   K. Tanaka, Y. Uchiyama, and S. Toyooka, "The mechanism of wear of polytetrafluoroethylene," *Wear*, vol. 23, no. 2, pp. 153–172, 1973.

[8]   M. K. Kar and S. Bahadur, "Micromechanism of wear at polymer-metal sliding interface," *Wear*, vol. 46, no. 1, pp. 189–202, 1978.

[9]   B. Bhushan, *Principles and applications of tribology*. John Wiley & Sons, 2013.

[10]   J. S. McFarlane and D. Tabor, "Adhesion of solids and the effect of surface films," *Proc. R. Soc. London. Ser. A. Math. Phys. Sci.*, vol. 202, no. 1069, pp. 224–243, 1950.

[11]   A. C. Moore and D. Tabor, "Some mechanical and adhesive properties of indium," *Br. J. Appl. Phys.*, vol. 3, no. 9, p. 299, 1952.

[12]   G. A. Somorjai and Y. Li, *Introduction to surface chemistry and catalysis*. John Wiley & Sons, 2010.

[13]   P. W. Atkins, "Physical Chemistry. 8th." Oxford University Press, 2006.

[14]   R. E. Johnson, R. H. Dettre, and J. C. Berg, *Wettability*. New York, NY: M. Dekker, 1993.

[15] R. J. Plunkett, "Tetrafluoroethylene polymers." Google Patents, 04-Feb-1941.

[16] W. E. Hanford and R. M. Joyce, "Polytetrafluoroethylene," *J. Am. Chem. Soc.*, vol. 68, no. 10, pp. 2082–2085, Oct. 1946.

[17] D. O'Hagan, "Understanding organofluorine chemistry. An introduction to the C-F bond.," *Chem. Soc. Rev.*, vol. 37, no. 2, pp. 308–319, 2008.

[18] Dupont, "Teflon PTFE ® Properties Handbook." .

[19] WS Hampshire, "TYPICAL PROPERTIES of PTFE," 2011. [Online]. Available: http://catalog.wshampshire.com/Asset/psg_teflon_ptfe.pdf.

[20] P. M. Stevens, *Polymer chemistry: an introduction*. Oxford University Press, New York, 1999.

[21] K. R. Makinson and D. Tabor, "The friction and transfer of polytetrafluoroethylene," *Proc. R. Soc. London. Ser. A. Math. Phys. Sci.*, vol. 281, no. 1384, pp. 49–61, 1964.

[22] C. M. Pooley and D. Tabor, "Friction and molecular structure: the behaviour of some thermoplastics," *Proc. R. Soc. London. A. Math. Phys. Sci.*, vol. 329, no. 1578, pp. 251–274, 1972.

[23] S. V Pepper, "Auger analysis of films formed on metals in sliding contact with halogenated polymers," *J. Appl. Phys.*, vol. 45, no. 7, pp. 2947–2956, 1974.

[24] D. Gong, B. Zhang, Q. Xue, and H. Wang, "Study on tribochemical interaction of metals or metal oxides with polytetrafluoroethylene by X-ray photoelectron spectroscopy," *J. Appl. Polym. Sci.*, vol. 41, no. 11-12, pp. 2587–2593, 1990.

[25] G. Deli, X. Qunji, and W. Hongli, "ESCA study on tribochemical characteristics of filled PTFE," *Wear*, vol. 148, no. 1, pp. 161–169, 1991.

[26] J. C. Wittmann and P. Smith, "Highly oriented thin films of poly (tetrafluoroethylene) as a substrate for oriented growth of materials," 1991.

[27] D. Fenwick, K. J. Ihn, F. Motamedi, J. Wittmann, and P. Smith, "Characterization of friction-deposited polytetrafluoroethylene transfer films," *J. Appl. Polym. Sci.*, vol. 50, no. 7, pp. 1151–1157, 1993.

[28] P. Bodoe, C. Ziegler, J. R. Rasmusson, W. R. Salaneck, and D. T. Clark, "Scanning tunneling microscopy study of oriented poly

(tetrafluoroethylene) substrates," *Synth. Met.*, vol. 55, no. 1, pp. 329–334, 1993.

[29]   P. Bodö and M. Schott, "Highly oriented polytetrafluoroethylene films: a force microscopy study," *Thin Solid Films*, vol. 286, no. 1, pp. 98–106, 1996.

[30]   D. W. Breiby, T. I. Sølling, O. Bunk, R. B. Nyberg, K. Norrman, and M. M. Nielsen, "Structural surprises in friction-deposited films of poly (tetrafluoroethylene)," *Macromolecules*, vol. 38, no. 6, pp. 2383–2390, 2005.

[31]   T. A. Blanchet and F. E. Kennedy, "Sliding wear mechanism of polytetrafluoroethylene (PTFE) and PTFE composites," *Wear*, vol. 153, no. 1, pp. 229–243, 1992.

[32]   G. Beamson, D. T. Clark, D. E. Deegan, N. W. Hayes, D. S-L Law, J. R. Rasmusson, and W. R. Salaneck, "Characterization of PTFE on silicon wafer tribological transfer films by XPS, imaging XPS and AFM," *Surf. interface Anal.*, vol. 24, no. 3, pp. 204–210, 1996.

[33]   S. M. Hsu and R. S. Gates, "Effect of materials on tribochemical reactions between hydrocarbons and surfaces," *J. Phys. D. Appl. Phys.*, vol. 39, no. 15, p. 3128, 2006.

[34]   X. Lu, K. C. Wong, P. C. Wong, K. A. R. Mitchell, J. Cotter, and D. T. Eadie, "Surface characterization of polytetrafluoroethylene (PTFE) transfer films during rolling–sliding tribology tests using X-ray photoelectron spectroscopy," *Wear*, vol. 261, no. 10, pp. 1155–1162, 2006.

[35]   J. Yu, S. H. Kim, B. Yu, L. Qian, and Z. Zhou, "Role of tribochemistry in nanowear of single-crystalline silicon," *ACS Appl. Mater. Interfaces*, vol. 4, no. 3, pp. 1585–1593, 2012.

[36]   J. J. Cole, C. R. Barry, R. J. Knuesel, X. Wang, and H. O. Jacobs, "Nanocontact electrification: patterned surface charges affecting adhesion, transfer, and printing," *Langmuir*, vol. 27, no. 11, pp. 7321–7329, 2011.

[37]   C. Gabler, E. Pittenauer, N. Dörr, and G. Allmaier, "Imaging of a tribolayer formed from ionic liquids by laser desorption/ionization-reflectron time-of-flight mass spectrometry," *Anal. Chem.*, vol. 84, no. 24, pp. 10708–10714, 2012.

[38]   H. T. Baytekin, B. Baytekin, J. T. Incorvati, and B. A. Grzybowski, "Material transfer and polarity reversal in contact charging," *Angew. Chemie*, vol. 124, no. 20, pp. 4927–4931, 2012.

[39] J. D. Schall, G. Gao, and J. A. Harrison, "Effects of Adhesion and Transfer Film Formation on the Tribology of Self-Mated DLC Contacts†," *J. Phys. Chem. C*, vol. 114, no. 12, pp. 5321–5330, 2009.

[40] T. A. L. Burgo and A. Erdemir, "Bipolar Tribocharging Signal During Friction Force Fluctuations at Metal–Insulator Interfaces," *Angew. Chemie*, vol. 126, no. 45, pp. 12297–12301, 2014.

[41] T. Onodera, M. Park, K. Souma, N. Ozawa, and M. Kubo, "Transfer-film formation mechanism of polytetrafluoroethylene: a computational chemistry approach," *J. Phys. Chem. C*, vol. 117, no. 20, pp. 10464–10472, 2013.

[42] T. Onodera, K. Kawasaki, T. Nakakawaji, Y. Higuchi, N. Ozawa, K. Kurihara, and M. Kubo, "Chemical reaction mechanism of polytetrafluoroethylene on aluminum surface under friction condition," *J. Phys. Chem. C*, vol. 118, no. 10, pp. 5390–5396, 2014.

[43] K. L. Harris, A. A. Pitenis, W. G. Sawyer, B. A. Krick, G. S. Blackman, D. J. Kasprzak, and C. P. Junk, "PTFE Tribology and the Role of Mechanochemistry in the Development of Protective Surface Films," *Macromolecules*, 2015.

[44] J. P. Youngblood and T. J. McCarthy, "Ultrahydrophobic polymer surfaces prepared by simultaneous ablation of polypropylene and sputtering of poly (tetrafluoroethylene) using radio frequency plasma," *Macromolecules*, vol. 32, no. 20, pp. 6800–6806, 1999.

[45] J. D. Miller, S. Veeramasuneni, J. Drelich, M. R. Yalamanchili, and G. Yamauchi, "Effect of roughness as determined by atomic force microscopy on the wetting properties of PTFE thin films," *Polym. Eng. Sci.*, vol. 36, no. 14, pp. 1849–1855, 1996.

[46] K. K. S. Lau, J. Bico, K. B. K. Teo, M. Chhowalla, G. A. J. Amaratunga, W. I. Milne, G. H. McKinley, and K. K. Gleason, "Superhydrophobic carbon nanotube forests," *Nano Lett.*, vol. 3, no. 12, pp. 1701–1705, 2003.

[47] T. Kamegawa, Y. Shimizu, and H. Yamashita, "Superhydrophobic Surfaces with Photocatalytic Self-Cleaning Properties by Nanocomposite Coating of TiO2 and Polytetrafluoroethylene," *Adv. Mater.*, vol. 24, no. 27, pp. 3697–3700, 2012.

[48] L. Feng, Z. Zhang, Z. Mai, Y. Ma, B. Liu, L. Jiang, and D. Zhu, "A super-hydrophobic and super-oleophilic coating mesh film for the separation of oil and water," *Angew. Chemie Int. Ed.*, vol. 43, no. 15, pp. 2012–2014, 2004.

[49] W. Hou and Q. Wang, "Stable polytetrafluoroethylene superhydrophobic surface with lotus-leaf structure," *J. Colloid Interface Sci.*, vol. 333, no. 1, pp. 400–403, 2009.

[50] D. Briggs and P. Seah, *Practical surface analysis: by auger and x-ray photo-electron spectroscopy*. Wiley, 1983.

[51] G. Beamson and D. Briggs, *High Resolution XPS of organic polymers , The Scienta ESCA 300 database John Wiley & Sons*, vol. 15. 1992.

[52] J. F. Watts and J. Wolstenholme, *An introduction to surface analysis by XPS and AES*, vol. 1. Wiley-VCH, 2003.

[53] J. F. Moulder, J. Chastain, and R. C. King, *Handbook of X-ray photoelectron spectroscopy: a reference book of standard spectra for identification and interpretation of XPS data*. Perkin-Elmer Eden Prairie, MN, 1992.

[54] J. F. Watts and J. Wolstenholme, "An Introduction to Surface Analysis by XPS and AES." Wiley Online Library, 1985.

[55] D. F. Mitchell, K. B. Clark, J. A. Bardwell, W. N. Lennard, G. R. Massoumi, and I. V Mitchell, "Film thickness measurements of SiO2 by XPS," *Surf. interface Anal.*, vol. 21, no. 1, pp. 44–50, 1994.

[56] C. Zhang, M. E. Grass, A. H. McDaniel, S. C. DeCaluwe, F. El Gabaly, Z. Liu, K. F. McCarty, R. L. Farrow, M. A. Linne, and Z. Hussain, "Measuring fundamental properties in operating solid oxide electrochemical cells by using in situ X-ray photoelectron spectroscopy," *Nat. Mater.*, vol. 9, no. 11, pp. 944–949, 2010.

[57] S. Kaya, H. Ogasawara, L.-Å. Näslund, J.-O. Forsell, H. S. Casalongue, D. J. Miller, and A. Nilsson, "Ambient-pressure photoelectron spectroscopy for heterogeneous catalysis and electrochemistry," *Catal. Today*, vol. 205, pp. 101–105, 2013.

[58] H. Bluhm, "4 - X-ray photoelectron spectroscopy (XPS) for in situ characterization of thin film growth," in *Woodhead Publishing Series in Electronic and Optical Materials*, G. Koster and G. B. T.-I. S. C. of T. F. G. Rijnders, Eds. Woodhead Publishing, 2011, pp. 75–98.

[59] I. Chorkendorff and J. W. Niemantsverdriet, "Catalyst Characterization," in *Concepts of Modern Catalysis and Kinetics*, 2005, pp. 129–166.

[60] S. Hisayoshi, O. Masanori, and K. Nakayama, "Surface roughness measurement by scanning electron microscope," *CIRP Ann. Technol.*, vol. 31, no. 1, pp. 457–462, 1982.

[61] D. Skoog, D. West, F. L. Holler, and S. Crouch, *Fundamentals of analytical chemistry*. Cengage Learning, 2013.

[62] F. C. Strong, "Theoretical basis of Bouguer-Beer law of radiation absorption," *Anal. Chem.*, vol. 24, no. 2, pp. 338–342, 1952.

[63] F. J. Holler, D. A. Skoog, and S. R. Crouch, "Principles of instrumental analysis," *Belmont: Thomson*, 2007.

[64] G. Binnig, C. F. Quate, and C. Gerber, "Atomic force microscope," *Phys. Rev. Lett.*, vol. 56, no. 9, p. 930, 1986.

[65] Y. Martin, C. C. Williams, and H. K. Wickramasinghe, "Atomic force microscope–force mapping and profiling on a sub 100-Å scale," *J. Appl. Phys.*, vol. 61, no. 10, pp. 4723–4729, 1987.

[66] R. W. Carpick and M. Salmeron, "Scratching the surface: fundamental investigations of tribology with atomic force microscopy," *Chem. Rev.*, vol. 97, no. 4, pp. 1163–1194, 1997.

[67] P. Eaton and P. West, "Atomic force microscopy, 2010." Oxford University Press, Oxford.

[68] B. Bhushan and C. Dandavate, "Thin-film friction and adhesion studies using atomic force microscopy," *J. Appl. Phys.*, vol. 87, no. 3, pp. 1201–1210, 2000.

[69] R. C. Hibbeler, "Mechanics of Materials (2000)." Prentice Hall, Upper Saddle River.

[70] H. Kuhn and D. Medlin, *ASM Handbook, Volume 08-Mechanical Testing and Evaluation*. ASM international Materials Park, OH, 2000.

[71] C. W. Bunn and E. R. Howells, "Structures of molecules and crystals of fluoro-carbons," 1954.

[72] G. Jintang, "Tribochemical effects in formation of polymer transfer film," *Wear*, vol. 245, no. 1, pp. 100–106, 2000.

[73] D. H. Buckley, *Surface effects in adhesion, friction, wear, and lubrication*, vol. 5. Elsevier, 1981.

[74] I. Jang, D. L. Burris, P. L. Dickrell, P. R. Barry, C. Santos, S. S. Perry, S. R. Phillpot, S. B. Sinnott, and W. G. Sawyer, "Sliding orientation effects on the tribological properties of polytetrafluoroethylene," *J. Appl. Phys.*, vol. 102, no. 12, p. 123509, 2007.

[75] N. L. McCook, D. L. Burris, P. L. Dickrell, and W. G. Sawyer, "Cryogenic friction behavior of PTFE based solid lubricant composites," *Tribol. Lett.*, vol. 20, no. 2, pp. 109–113, 2005.

[76] I. Tzanakis, M. Conte, M. Hadfield, and T. A. Stolarski, "Experimental and analytical thermal study of PTFE composite sliding against high carbon steel as a function of the surface roughness, sliding velocity and applied load," *Wear*, vol. 303, no. 1, pp. 154–168, 2013.

[77] J. T. Shen, Y. T. Pei, and J. T. M. De Hosson, "Structural changes in polytetrafluoroethylene molecular chains upon sliding against steel," *J. Mater. Sci.*, vol. 49, no. 4, pp. 1484–1493, 2014.

[78] B. Schrader and W. Meier, *Raman/infrared atlas of organic compounds*. VCH Weinheim, 1989.

[79] A. Lafuma and D. Quere, "Superhydrophobic states," *Nat Mater*, vol. 2, no. 7, pp. 457–460, Jul. 2003.

[80] N. Maeda, N. Chen, M. Tirrell, and J. N. Israelachvili, "Adhesion and friction mechanisms of polymer-on-polymer surfaces," *Science (80-.).*, vol. 297, no. 5580, pp. 379–382, 2002.

[81] N. Chen, N. Maeda, M. Tirrell, and J. Israelachvili, "Adhesion and friction of polymer surfaces: the effect of chain ends," *Macromolecules*, vol. 38, no. 8, pp. 3491–3503, 2005.

Appendix

1. Monitoring Tribological Transfer onto Glass Surfaces

In addition to the non-coated and polymer-coated silicon oxide surfaces which were slid with PTFE tip, tribological transfer was also performed on glass (microscope slide) surfaces under ambient conditions and using the same experimental setup which was shown in Figure 9. Before the transfer, glass surfaces were cleaned with acetone and deionized water, then dried in air. Because glass surfaces are mostly composed of silicon dioxide, tribological transfer of PTFE was also expected to occur onto these surfaces. F1s areal map of a PTFE slid glass surface shown within Figure 38 met our expectations. In specimens contacted with PTFE tip, transfer was observed similar to silicon oxide surfaces, but controlling the patterns to be transferred was challenging due to the slippery characteristic of the glass surface.
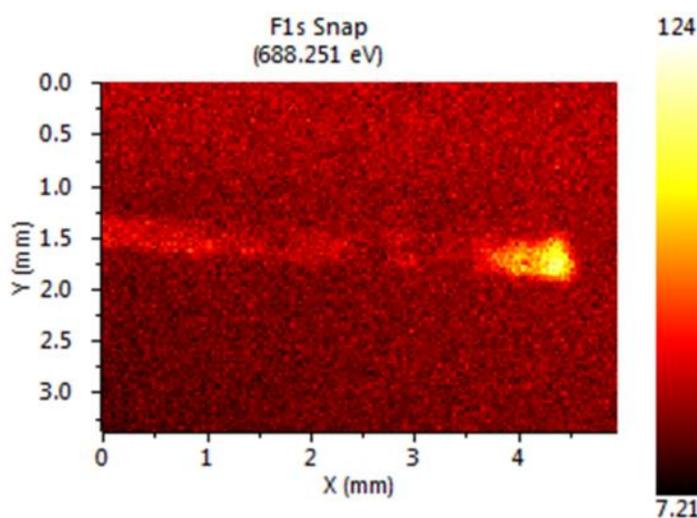

Figure 38. F1s areal map of a glass (microscope slide) surface which was slid with PTFE.

2. Acidic and Basic Treatment of Silicon Surfaces

Although observation of some triboelectrical changes occurring on treated silicon oxide surfaces with aqueous acidic and basic solutions was reported in literature[36], we could not observe any significant difference as a result of these treatments. As a procedure for the treatment of silicon surfaces (shown in Figure 39), after dipping into aqueous solutions of 1M HCl or NaOH for an hour, they were soaked in deionized water for an additional hour.
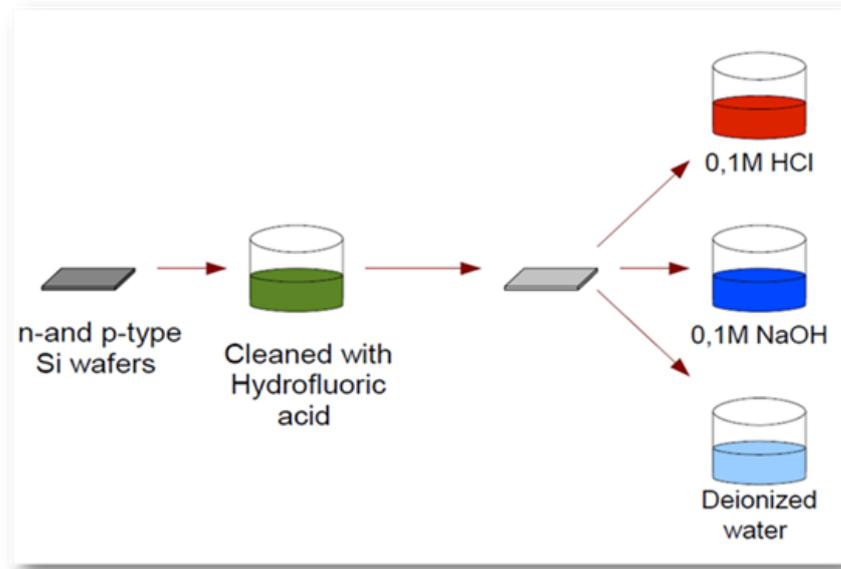

Figure 39. Schematic representation of the procedure used for the treatment of silicon surfaces

As illustrated in Figure 40, a single line which was imparted through sliding PTFE on differently treated surfaces is observable in all specimens. Although slight differences were detected in F1s intensities of lines as also represented in the color bar attached next to the map, they were thought to be not significant.
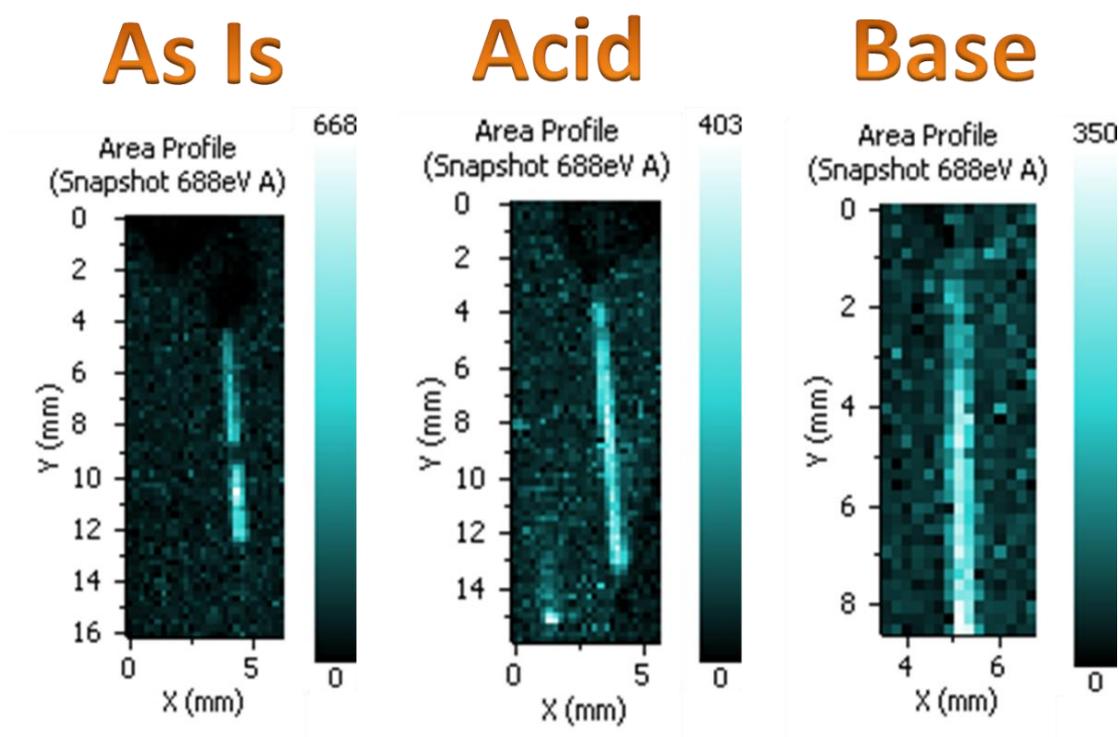
Figure 40. F1s areal maps of a) as is b) acid-treated c) base-treated silicon surfaces which was slid with PTFE

In addition to this, silicon surface treatment dipping into aqueous acid and base solutions was also utilized for thermally oxidized silicon samples. As shown in Figure 41, areal maps and on-line high resolution spectra taken within Si2p, F1s and C1s regions, verified that there was no significant change again in both characteristics of implemented lines and nature of the transfer in thermally-oxidized specimens.

PTFE/on/HCl-treated SiO$_x$

a) Si2p   b) F1s   c) C1s
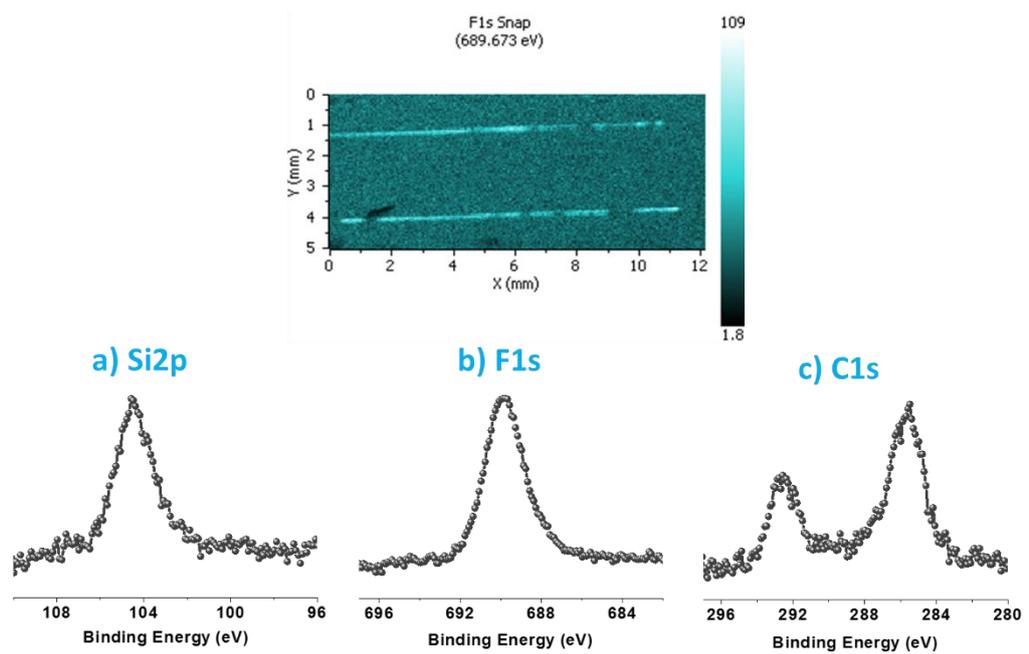
PTFE/on/NaOH-treated SiO$_x$
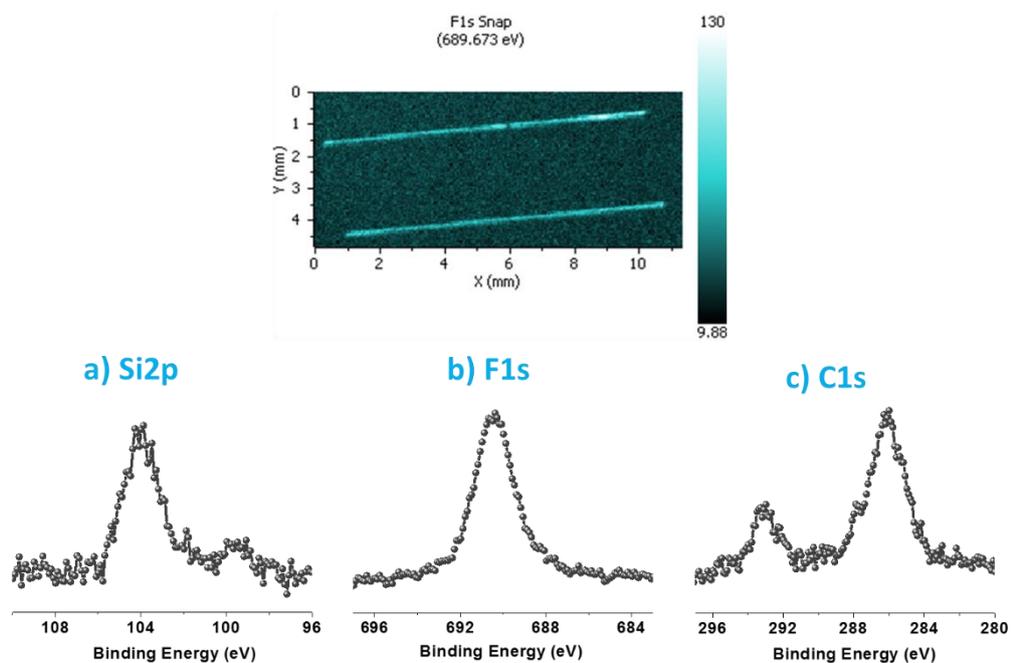

a) Si2p   b) F1s   c) C1s

Figure 41. F1s areal maps of acid and base-treated, PTFE-slid silicon oxide surfaces with high resolution spectra taken on a random point above the line