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On the possibility of using low-energy electron stimulated desorption of ions as a surface probe: Analysis of Au substrates

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ABSTRACT

We explore the possibility of using low-energy (0–50 eV) electron stimulated desorption (ESD) of ions, analyzed by time-of-flight (TOF) mass spectrometry, as a surface analysis technique. As a first step, we measure the mass spectra from ions emanating from gold substrates prepared for molecular self-assembly by two different methods: cleaning with sulfochromic acid (CrO_3/H_2SO_4) and exposure to UV/O_3. Modifications of the yields of desorbed anions and cations as functions of incident electron energy provide information on the presence and the chemical nature of contaminants present on the Au surface, either before or after cleaning. Upon cleaning, the decrease in intensity of the yield functions of certain desorbed anions and cations associated with organic molecules confirms that both techniques are efficient in removing organic contaminants. On the other hand, other ESD signals increase or only appear by either cleaning procedure. This finding demonstrates how these cleaning techniques can contaminate Au surfaces with species, such as acid residues and nitrogenized organic molecules. Such observations have never been reported before with other methods of surface analysis. The present results strongly suggest that ESD of ions should be considered as a potential sensitive tool to complement surface analysis by other well-established methods.

1. Introduction

Low-energy electron stimulated desorption (ESD) is a powerful and very sensitive mass spectrometry technique to study the effects of low-energy electrons (LEEs) on physisorbed or chemisorbed molecular thin films by measuring the ionic fragments desorbed from the irradiated surface. ESD has been used in several fields such as polymer science [1,2], radiation chemistry [3–5], radiobiology [6–8] and astrochemistry [9,10]. The low-energy ESD technique consists of irradiating a surface with LEEs of varying energies (e.g., 1–20 eV) and monitoring the amount of specific desorbed ions with a mass spectrometer; the ion desorption yields measured as a function of electron energy are termed *yield functions*.

At LEE energies below 30 eV, electron interactions with a molecule can be described in terms of non-resonant (direct) or resonant scattering [11]. Resonance scattering leads to the formation of a transient negative ion (TNI), resulting from the temporary attachment of an electron to a molecule. This anion state occurs at a specific resonance energy, corresponding to a given orbital configuration of the molecule. If the TNI is dissociative in the Franck–Condon region and its lifetime is long enough ($>10^{-14}$ s) to permit dissociation before electron emission by autodetachment, dissociative electron attachment (DEA) can occur giving an anionic fragment and neutral radical(s), i.e.,

$$AB + e^- \rightarrow AB^- \rightarrow A^- + B^\bullet. \qquad (1)$$

Non-resonant scattering involves direct energy transfer from an incident electron to a molecule, and can lead to the fragmentation of the molecule into neutral and/or ionic species. Incident electrons scatter inelastically with cross sections varying smoothly with their kinetic energy (i.e., impact energy), resulting to a monotonic rise in the yield functions with electron energies from 12 to 15 eV until a broad maximum is reached around 30–60 eV. Below 30 eV, two direct processes are known to produce ionic fragments. Dipolar dissociation (DD) is usually non-resonant and can produce a significant signal of stable anions with sufficient energy ($\geq$1 eV) to escape the induced polarization potential at the surface. Energy transfer from the incoming electron to the molecule produces an electronically excited dissociative state, which dissociates into positive and negative fragments:

$$AB + e^- \rightarrow AB^* + e^- \rightarrow A^- + B^+ + e^-. \qquad (2)$$

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The other process, which is called dissociative ionization (DI), does not produce anions contrary to DEA and DD. The DI process involves an electronic transition of the molecule toward a dissociative excited cationic state by non-resonant inelastic scattering of the incident electron:

$$AB + e^- \rightarrow AB^{*+} + 2e^- \rightarrow A^\bullet + B^+ + 2e^-. \quad (3)$$

In this work, two Au surfaces designed for self-assembling were cleaned by different treatments and studied by ESD to evaluate its potential as a surface analysis technique. Self-assembling is widely used to produce well-ordered, dense and stable thin films [12]. Self-assembled monolayers (SAMs) are well-suited for studies and applications in nanotechnology [12], surface science [13] and biology [14], because they are easy to prepare, the chemistry of the functional heading groups can be chosen, and they are resistant against chemicals [14,15]. SAMs are usually produced by immersing a metallic substrate into a solution of organic molecules with specific anchors that permit chemical bonding of the molecule to the substrate. The most common anchors are silanes, phosphonates and thiols, but among the possible anchor/metal combinations, the thiol functional group on gold (–SH/Au) is the most widely used. To produce a high bonding rate in SAM fabrication, the Au substrate must carefully be cleaned. The Au surface is subject to several contaminants upon exposure to common atmospheric conditions, which affects the binding kinetics of thiols in addition to their electrochemical properties [16]. Several techniques have been developed to clean Au surfaces: ultraviolet/ozone (UV/O_3), O_2 plasma, KOH + H_2O_2 solution, KOH with potential sweep, sulfochromic acid solution, piranha solution, H_2SO_4 with potential cycling, HCl potential cycling, and HNO_3 + HCl solution. Among these techniques, UV/O_3 and H_2SO_4 solutions (i.e., sulfochromic acid and piranha solutions) are among the most widely reported for fabrication of SAMs, and have been chosen for this work.

The UV technique has been utilized since 1972 as a method of depolymerizing photoresist polymers [17]. Combined with ozone, this technique has been shown to be an effective low-cost dry method to rapidly and easily remove organic contaminants (e.g., oils, greases and contamination adsorbed during prolonged exposure to air) from Au surfaces in normal air and temperature conditions [18]. The UV/O_3 cleaning mechanism involves photosensitized processes that oxidize organic molecules (e.g., ethanol, glycine, and glycerol) and some inorganic molecules (e.g., potassium or nickel cyanides). Subsequently, these oxidized molecules dissociate by further oxidation into volatile compounds such as CO_2, CO, H_2O and N_2 [18–20]. After being cleaned by UV/O_3, the Au surface exhibits a highly oxidized state with a stoichiometry close to Au_2O_3, as reported in numerous studies [20–23]. On the other hand, inorganic contaminants, such as salts and dust, cannot be removed by UV/O_3 [18]; washing the Au surface after the UV/O_3 cleaning with ultra-pure water is thus necessary.

Cleaning of an Au surface by a mixture of sulfuric acid and hydrogen peroxide ($H_2SO_4 + H_2O_2$), known as piranha solution, also involves oxidation of organic contaminants via two distinct mechanisms that operate under different rates: a faster process of dehydration that results in the carbonization of organic molecules, especially carbohydrates, and a second process that converts H_2O_2 to an aggressive oxidizing agent ($H_2SO_4 + H_2O_2 \rightarrow H_3O^+ + HSO_4- + O$) capable of dissolving the carbonized organic molecules. The cleaning by such solutions results once again in an oxidized Au surface, as observed by X-ray photoelectron spectroscopy (XPS) [16,24,25], via different reactions producing AuO, AuO_2, $Au(OH)_3$, AuOOH and/or Au_2O_3 [24,26]. One drawback of such a cleaning technique is that even contact of Au with a piranha solution of 30 s can damage significantly the Au surface topography. Kang and Rowntree [26] have shown using scanning tunneling microscopy (STM) that piranha solution treatments for less than 5 min can cause delamination of the Au/mica surface, the introduction of pinholes into the Au layer, and a significant modification of the Au morphology by the deposition of Au particles onto the surface. The authors also explored the use of sulfochromic acid (CrO_3/H_2SO_4) as a cleaning agent. They found that the surface etching process is far more controlled and less aggressive than that in piranha solutions [26].

The quality of the cleaning methods of Au surfaces has been characterized not only by XPS [16,20–23,27–30] but also by a large variety of other techniques including cyclic voltammetry [16,19,31], atomic force microscopy (AFM) [16,24,27], contact angle measurements [19,32], scanning force microscopy (SFM) [19], Auger electron spectroscopy (AES) [27], ion scattering spectroscopy (ISS) [21], low-energy electron diffraction (LEED) [20], temperature programmed desorption (TPD) [20], scanning electron microscopy (SEM) [28] and STM [26]. As the cleaning of Au surfaces by UV/O_3 and sulfochromic acid treatments are well understood, they can serve to explore the feasibility of using low-energy ESD as a new surface analysis technique. Desorption of anions and cations under LEE irradiation has been measured from uncleaned Au surfaces and from surfaces treated by the two methods. As long as the atomic composition of a mass peak can be unambiguously determined, modifications in the ESD yield function of a given mass gives, with a significant sensitivity, information on the presence and the chemical nature of a contaminant on the Au surface before and after cleaning.

2. Materials and methods

The Au samples were prepared by vacuum evaporation of gold (99.99% purity; TD Canada Trust) at a rate of 1–10 Å/s onto freshly cleaved mica sheets (Ted Pella Inc.). The Au deposition is based on the protocol of DeRose et al. [33] and was performed in an all-metal turbo molecular-pumped evaporation system. The thickness of the deposited Au films was evaluated at ~200 nm with a predominant Au(1 1 1) structure owing to heating to 300 °C before, during, and after evaporation of the metal. For this study, the Au samples, cut to a size of $1.2 \times 1.2\,cm^2$, were cleaned by one of the two techniques, i.e., UV/O_3 exposure and acid wash. The protocol of UV/O_3 cleaning is based on our previous work [7]. Prior to UV/O_3 exposure, the samples were rinsed with methanol and Millipore water ($R > 18\,M\Omega$). The samples were then exposed to UV light produced by an 18.4 W STER-L-RAY® U-shaped O_3-producing lamp from Atlantic Ultraviolet Corporation, for three periods of 20 min in ambient air. After each UV/O_3 treatment, the samples were rinsed with Millipore water and dried with pressurized N_2. For the second cleaning technique, the surface of Au films was covered with sulfochromic acid solution (i.e., chromium trioxide in concentrated H_2SO_4) from Fisher Scientific. After 40 s, the acid solution was wiped away, the samples were thoroughly rinsed 5–10 times alternating with Millipore water and methanol, and then dried under a flow of N_2. Immediately after the cleaning, the samples were mounted onto copper sample carriers and then transferred into the load-lock coupled to the UHV ESD chamber. They were degassed within the load-lock chamber for at least 12 h prior to their transfer into the ESD chamber.

The ESD measurements were performed using a time-of-flight (TOF) mass spectrometer (Kore-5000 Reflectron), housed in an UHV system reaching a base pressure of 5×10^{-10} Torr [34]. Samples were bombarded with a pulsed LEE beam (800 ns pulses at a repetition frequency of 5 kHz) from a Kimball Physics ELG-2 gun with an incident current of ~2.5 nA and at an angle of 45° with respect to the sample surface normal. The electron beam spot size has been evaluated to ~3 mm^2. Immediately after each LEE pulse, a negative