Effect of ITO surface properties on SAM modification: A review toward biosensor application

Md. Zaved Hossain Khan

Cogent Engineering (2016), 3: 1170097
**MATERIALS ENGINEERING | REVIEW ARTICLE**

**Effect of ITO surface properties on SAM modification: A review toward biosensor application**

Md. Zaved Hossain Khan*

**Abstract:** The aim of this review is to discuss the effect of physical and chemical properties of Indium tin oxide (ITO) thin film on its self-assembled monolayer (SAM) modification, as well as device performance toward biosensor applications. The emphasis is on surface morphology studies of the thin films in order to provide connecting points between surface properties with the broader field of material science of ITO. The morphology of SAM film deposited on it directly affects by the properties of these prepared ITO film. Thus, it is a topic of interest to study the influence of physicochemical properties of this film on device fabrication and applications as biosensor platform.

**Keywords:** ITO electrode; surface characterization; biosensor; self-assembled monolayer

1. **Introduction**

Indium tin oxide (ITO) is a well-known electrode material and widely used for its unique optoelectronic properties. There has been a growing technological interest in materials with electrically conductive and optically transparent. ITO thin film is one of the most popular thin films and used in several applications including optoelectronic and electrochemical applications due to its very high transmittance and conductivity (Chopra, Major, & Pandya, 1983). The electrochemical and physical
properties of ITO electrode are very stable; hence, it is widely used as electrode substrate for different purposes (Hayashi, Iwasaki, Horiuchi, Sunagawa, & Tate, 2005; Sun & Gillis, 2006; Zhang, Au, Zhu, & O’Shea, 2004; Zhang, Kambayashi, & Oyama, 2005).

Over the last few decades, the interest in ITO (as substrate adhesion) is increasing rapidly due to its excellent properties and prominent characteristics. More recently, ITO electrodes widely used as transparent semiconductor in the field of many electro-optical devices (Armistead & Thorp, 2001; Corry, Uilk, & Crawley, 2003; Qiu et al., 2003; Shipway, Katz, & Willner, 2000; Tominaga, Kumagai, Takita, & Taniguchi, 1993; Willner, Lapidot, Riklin, Kasher, & Zahavy, 1994; Zhan, Alvarez, & Crooks, 2002; Zheng et al., 2004), e.g. electrochemical biosensors (Armistead & Thorp, 2001), optical sensors (Shipway et al., 2000), LCD screens, electron transfer of protein (Tominaga et al., 1993), optical windows, etc. In biosensor applications, ITO surfaces are usually modified with silane monolayer to control biomolecule immobilization (Corry et al., 2003; Justin Gooding, Mearns, Yang, & Liu, 2003; Niwa, Homma, & Osaka, 2004).

A highly degenerated semiconductor like ITO has so many dopants that the electron concentration in the conduction band is comparable with the density of states in the band. The hole concentration in the valence band is comparable in the case of P-type material. During the film growth, degeneracy caused with the creation of the oxygen vacancies and substitutional tin dopants.

Due to the prominent characteristics of ITO electrodes such as excellent optical transparency, high conductivity, these electrodes have attracted increasing interest recently and widely used for their excellent substrate adhesion and electrochemical properties. Because of those stable characteristics, ITO film has been widely used in industrial applications. Sputtering is the most common deposition technique and widely investigated for large-scale deposition setups for ITO thin film production. By this method, low-cost deposition system, good film performances, and high sputtering rate could be achieved.

For immobilization of biomolecules, it is necessary to modify the ITO surface with silane reagents under well condition. Basically in early stage, ITO films were used as electrodes for spectroelectrochemical measurements due to their conductivity and transparency. Nowadays, due to critical importance of electron transfer and surface properties, ITO electrodes have been employed in electroanalytical sensors. For making electro-optical devices like; LCD screens, CMOS imagers etc. ITO electrodes are widely used as transparent semiconductor.

2. Modification of ITO electrode

2.1. Monolayer modification

Self-assembled monolayer (SAM) usually used to control the physical and chemical properties of solid surface (Niwa et al., 2004). Considering electrochemistry, the term SAM is very common in designing selective electrode for electroanalytical applications. SAM of organic and biological molecules on metal surfaces are important in many application fields, ranging from sensors (Mizutani, 2008; Wackerbarth et al., 2005) to nanostructured devices (Love, Estroff, Kriebel, Nuzzo, & Whitesides, 2005) and have been of interest for last few decades. SAM represents a promising strategy to functionalize noble metal surfaces by forming ordered organic films leading to molecular architectonic which continue to serve as major techniques for the fabrication of supramolecular structures (Madueno, Räisänen, & Silien, 2008; Theobald, Oxtoby, Phillips, Champness, & Beton, 2003). On the other hand, SAM-based techniques are of particular importance in molecular recognition system on electrode surface, and offer a vehicle for investigation of specific interactions at interfaces with their functional properties that bear promise for technological applications (Justin Gooding et al., 2003; Mizutani, 2008; Niwa et al., 2004; Wackerbarth et al., 2005; Love et al., 2005). Figure 1 represents the SAM-modified ITO electrode surface in light emitting diodes (OLEDs) and organic thin film transistors (OTFTs) applications.
Several studies have been done on attachment of silane molecule on ITO surface at different conditions \cite{Asanov1998, Jee2006, Madueno2008, Theobald2003}. For fabricating biosensors, functionalization and patterning of silane SAMs is very popular method due to its simple preparation, reproducibility, and stability. The characterization of SAM of silane on ITO is important to study their interaction on the surface. The attachment of organic molecules \cite{Moses1975} and mixed SAMs of different functionality \cite{Bain1988} shows formation of monolayer on ITO surface. Trialkoxysilanes has been used mostly by means of covalent attachment for activating ITO surfaces \cite{Asanov1998, Jee2006, Madueno2008, Theobald2003}. Other researchers have used SAM-modified ITO electrode for detecting nucleic acids \cite{Napier1997}, heteropolyacid \cite{Oh1999}, nanometric components \cite{Gardner1995}, etc. Nowadays, extensive studies are going on to elucidate the response mechanism of SAM on different inorganic surface and their electrochemistry \cite{Vilan2002}. Specially, the surface characterization is very important to examine the physiochemical properties of the surface before and after SAM modification. SAM of different silane molecules onto ITO surface is shown in Figure 2.

Several researchers used carboxylic and phosphonic acids onto ITO electrode instead of the adsorption of thiols on gold that effectively enable the controllable connection of nanometric components. For attaching organic and biological molecules onto ITO surface, functionalized alkyl silanes (aminopropyltrimethoxysilane; APTES) are widely used. Khan, Nakanishi, and Osaka \cite{Khan2011} used APTES-modified ITO electrode for biosensor application as shown in Figure 3.

Due to high surface roughness of ITO electrode, small number of studies have been reported on silane chemistry for attaching alkyl chains onto its surface. Even though this conducting and transparent substrate is an attractive film for silane attachment, the characterization of SAMs on ITO surface and its reproducible preparation becomes difficult due to high surface roughness of the
Several researchers have studied mixed-component SAMs with different functionality and chain length, of which covalently attaching organic molecules was also carried out. To minimize the possibility of polymer formation, many of them were careful to employ dry conditions during using trichloro and triethoxysilanes. To confirm monolayer formation, layer thickness measurement and its coverage test were done.

3-Aminopropyltriethoxysilane (APTES) is one of the common functionalized alkyl silanes used to prepare amine-functionalized SAM on ITO surface (Muthurasu & Ganesh, 2012; Vilan et al., 2000). A negatively charged NH₂ terminated monolayer creates on the surface through the protonation of amino group that effectively reduces the device work function (Khan, Nakashi, & Osaka, 2011; Shaya, Einati, Fishelson, Shacham-Diamand, & Rosenwaks, 2010).

Due to the simple preparation method of silane SAM films, it is widely used to immobilize proteins, enzymes onto the semiconductor surfaces for fabricating biosensors. Moore, O’Connell, and Galvin (2006) had developed DNA sensor with silane-modified ITO electrode and described its covalent attachment chemistry which is shown in Figure 4. For the late immobilization of biomolecules such as antibodies, enzymes, DNA, etc., organic SAMs on the solid surface are one of the most suitable functional interlayers.

![Figure 2. Chemical structures of various silane molecules such as phenyl trimethoxysilane (PHMS), octadecyltrimethoxysilane (ODTMS), methyl trimethoxysilane (MTMS), and 3-mercaptopropyltrimethoxysilane (MPTMS) used for SAM formation on ITO electrodes.](image)

Source: Reproduced with permission of Elsevier (Muthurasu & Ganesh, 2012).

![Figure 3. Schematic representation of stepwise modification of ITO electrode with 3-Aminopropyltriethoxysilane (APTES) and disuccinimidyl suberate (DSS) for the detection of several biomolecules reported by Khan et al. (2011).](image)
Both spectroscopic and microscopic techniques are widely used to characterize the SAMs on electrode surface. Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), Infrared (IR), Raman, Atomic force microscopy (AFM), Scanning electron microscopy (SEM), Scanning probe microscopy (SPM), etc. have been used for the mentioned purposes. Scanning tunneling microscopy (STM) and AFM study combined used for through description of the SAMs structure on the electrode surface.

2.2. Modified ITO electrode as a sensor

Detection of biomolecules that release from living cell is of great interest in the view of biological and medical science from last few decades. Different types of microelectrodes have been used as amperometric/potentiometric sensors for this purpose of molecule detection. Modification of ITO electrode surface is one of the efficient ways to increase its electroanalytical activity to work toward biosensor development. For the detection of transmitter released from single cells, different types of midwifed microelectrodes are used as amperometric/potentiometric sensors. Due to its good photo-penetrability and high electrical conductivity, ITO electrode has been widely used for electrochemical detection of biomolecules. To increase the electroanalytical activity of ITO electrodes, usually surface modification is performed.

Wide range of surface can be created by immobilization of biomolecules onto semiconductor surface and used as a key step in biosensor applications (Armistead & Thorp, 2000; Fang, Ng, & Li, 2003; Ferreira, Fiorito, Oliveira, & Córdoba de Torresi, 2004; Prieto-Simon, Campas, & Marty, 2008; Ruan, Yang, & Li, 2002). Chemically modified ITO electrode has been widely used as working electrode for the detection of biomolecules. Osaka et al. observed enantioselective potential response for
tryptophan with human serum albumin (HSA)-modified ITO electrode (Matsunaga, Ueno, Nakanishi, & Osaka, 2008) as shown in Figure 5. Usually, bio-components like enzyme, tissue, antigen-antibody, etc. attached to the electrode surface that functions as the biological recognition elements.

Chemically modified electrode (CME) biosensor is also used for the recognition of biological elements or biochemical receptor (Durst, Baumer, Murray, Buck, & Andrieux, 1997). Hyperbranched gold nanoparticles are used for the modification of ITO electrode to detect biomolecules (Tiwari, Aryal, Pilla, & Gong, 2009). IUPAC report (Thevenot et al., 1999) described the CME modification technique, classification and its terminology. Ion-selective electrodes (ISEs) are generally used in potentiometric formats (Buck, 1978; Ross, Riseman, & Krueger, 1973). CMEs are widely used for analytical applications due to its ability to manipulate the molecular architecture of the bulk matrix of an electrode and created powerful opportunities for electroanalysis (Aboul-Enein & Wainer, 1997; Berthier, Buffeteau, Léger, Oda, & Huc, 2002; Lin, Hu, Xu, & Pu, 2002; Massolini, Temporini, & Calleri, 2008; Millot, 2003; Schröer et al., 2007; Stefan, van Staden, & Aboul-Enein, 2001; Zhou, Nagaoka, Yu, & Levon, 2009).

Numerous studies have been reported on the modified ITO electrode sensors by highlighting its electronic and optical properties. Chemical modification of ITO electrode is a prerequisite for biosensor application that usually done with organic anchor molecules. In most previous reports, silane molecules are commonly used for surface attachment on the hydroxylated ITO surface as anchor molecules through SAM process. The end part of the silane molecule needs to be activated for the immobilization of biomolecules or their ligands by chemical coupling reaction. Carboxylic and phosphonic acids and amines are also used for organic layer formation on ITO surface as other

Figure 5. Schematic diagram of SAM modification of ITO electrode (ITO/APTES/DSS/HSA) (top); and time dependence of the potential shift after injection of Trp solution (bottom).

Source: Reported by Osaka et al. toward chiral sensing by modified ITO. Reproduced with permission of Elsevier (Matsunaga et al., 2008).
modification procedures. Although the chemical modification of ITO electrode is an attractive approach, their functionality and characterization study is always in terms of further study. Table 1 represents different functional groups that are used to modify ITO electrode for the immobilization of biomolecules.

Gold, silicon, and ITO (Budnikov, Evtyugin, Budnikova, & Al’fonsov, 2008; Izake, 2007; Trojanowicz & Wcislo, 2005) electrodes are widely used due to easiest method of fabrication for chiral molecule detection with high sensitivity (Bakker & Qin, 2006; Horváth et al., 1997; Junxiang, Sato, Umemura, & Yamagishi, 2005; Yasaka, Yamamoto, Kimura, & Shono, 1980). But sometimes, the bulky molecules reduce this sensitivity (Grieshaber, MacKenzie, Vörös, & Reimhult, 2008). Attachment of various organic molecules on bare ITO electrode surfaces has demonstrated that it is rapid and directed electrochemically to precise positioning of adsorbent molecules. In biosensor applications, several functional molecules have primary amines; therefore, the attachment of primary amines seems very useful technique. Sometimes, primary amine groups attach on to bare ITO electrode surface by direct electrochemical modification. M.Z.H. Khan et al. have detected several biomolecules with SAM-modified ITO electrode shown in Figure 6.

### Table 1. Major functional tailgroups for surface functionalization (Kim & Kang, 2008)

| Functional groups | Surface property | Interaction or reaction with biomolecules |
|-------------------|------------------|------------------------------------------|
| R–(CH₂)ₙ–NH₃⁺ (+) | Charge           | Charge-charge interaction                 |
|                   |                  | EDC-mediated chemical bonding with carboxyl group (R–COOH) of biomolecules |
|                   |                  | Glutaraldehyde-mediated chemical bonding with amine group (R–NH₂) of biomolecules |
| R–(CH₂)ₙ–COO⁻ (−) | Charge           | Charge-charge interaction                 |
|                   |                  | EDC-mediated chemical bonding with amine group of biomolecules |
| R–(CH₂)ₙ–CH₃      | Hydrophobic      | Hydrophobic interaction                   |
| R–(CH₂)ₙ–CHO      | Aldehyde NHS     | Chemical bonding with amine group of biomolecules |
| R–(CH₂)ₙ–O⁻       | Maleimide        | Chemical bonding with sulfhydryl group (R–SH) of biomolecules |
| R–(CH₂)ₙ–O–CH₂–CH₂ | Epoxy            | Chemical bonding with hydroxyl (R–OH), amine and sulfhydryl groups of biomolecules |
| R–(CH₂)ₙ–S⁻       | Biotin           | Specific interaction with avidin or streptavidin |
| R–(CH₂)ₙ–O–OH     | Ethylene glycol  | Preventing the non-specific adsorption of biomolecules |
CME has the distinguished feature of having quite thin film that can be formed by bonding of selected chemicals on the electrode surface which is rational, chemically designed manner comparing other electrodes. Biosensor can detect picomolar range analyte concentration by specific binding interactions. Protein or cells have a tendency to adsorb onto interfaces without specific receptor-recognition interaction between substrates and biological samples.

Due to surface properties of ITO electrode, the reproducibility of SAM preparation and its characterization is sometimes difficult task (Rasmusson, Bröms, Birgerson, Erlandsson, & Salaneck, 1996). For achieving reproducibility of conductive surface like ITO, surface characterization, and details, surface chemistry study is essential. Optimizations of surface controlling parameters are important factor for the development of biosensor.

For the reproducibility of the measurement, it’s always important to examine the factors that can affect electrode–analyte interface performance. Changes in surface composition can easily affect its affinity and interaction properties. Controlling of electrochemical and physiochemical properties of surface is important task for designing nano-device electrode. During deposition process, care should have taken to achieve optimum properties and to reduce manipulation.

3. Surface properties of ITO electrode

3.1. Surface roughness

Surface morphology including physical, chemical, mechanic properties plays an important role to control the efficiency of a device. Among them, surface roughness in an important parameter, since the behavior of an electrochemical device depends on surface morphology (Bourlange et al., 2008; Dulub, Diebold, & Kresse, 2003; Golovanov et al., 2005; Goniakowski, Finocchi, & Noguera, 2008; Milliron, Hill, Shen, Kohn, & Schwartz, 2000; Noguera, 2000; Park, Choong, Gao, Hsieh, & Tang, 1996; Zhou et al., 2008). Surface roughness plays an important role in controlling surface chemical composition. Surface chemical composition can be easily altered by changing roughness properties. Several techniques are used to determine the surface roughness properties. AFM is a method widely used to measure the surface roughness. Kelvin probe force microscope (KFM) is used to measure surface work function and is an important parameter to determine the electrode role in device performance and SAM modification. In particular, when ITO electrode used as electrochemical device, surface
morphology and chemical properties plays important role and needs to optimize for achieving highest performance. Figure 7 shows AFM images of ITO surface with different roughness properties.

The measurement of finely spaced surface irregularities is usually termed as surface roughness (SR), which is a numerical value of the mean roughness height. The physical, mechanical, chemical behavior of the surface is often determined by the configurational characteristics of the surface, where roughness plays an important role. Considering the use of ITO films as electrochemical device, the behavior depends on the morphology of the rough surfaces and it is an important parameter to be considered.

AFM is a widely used instrument to provide details of surface roughness parameters. Specially, average surface roughness ($S_a$), surface skewness ($S_{sk}$), and surface kurtosis ($S_{ku}$) are the important parameters to describe the height distribution histogram of surface (Ballarin, Cassani, Gazzano, & Solinas, 2010; Kim et al., 2003; Stout et al., 1993). M.Z.H. Khan et al. observed several spikes on ITO surface that was reported as low roughness shown in Figure 8. The difference in near-surface composition is related with surface roughness differences and considered to affect the properties of ITO (Brumbach et al., 2007; Morales & Diebold, 2009; Morales, He, Vinnichenko, Delley, & Diebold, 2008; Walsh & Catlow, 2010). Therefore, the performance of electrochemical device like ITO depends on its surface morphology and can affect the characteristics of the thin film deposited on it. Details of surface roughness include not only average roughness but also height distribution coefficient. Average deviation of the measured $z$-values from the mean plane can describe the amplitude of roughness parameters. Gaussian height distribution also plays an important role for measuring local peak height distribution that is related with sharpness of the surface.

The Gaussian height distribution term is very common method used to determine the surface morphology and can be calculated by the surface kurtosis and skewness value. In Figure 9, surface height distribution of several types of ITO electrode was shown. Usually, AFM provides the statistical analysis of the surface roughness features. Considering the fabrication of electrochemical device, the control of surface morphology is very important term and widely studied problem in recent years. The device performance is strongly affected by the negative effects of uneven surface that affects the morphology of the thin film. Over the last few decades, many researchers have studied the relationship between the structural and optical properties of ITO electrode with its surface morphology.

### 3.2. Surface composition
The performance of ITO electrode is extremely sensitive to its surface condition. The study of the relationship between surface conditions and different properties of ITO electrode is subjected to various treatments. Several researchers reported the effect of surface chemical composition change on the electrochemical properties of ITO electrode (Morales & Diebold, 2009).
The surface composition of ITO electrode, especially In:Sn ratio effectively changes the electrochemical properties of the electrode due to surface Fermi level electronic properties by controlling the surface potential as well as its work function. ITO electrode with different surface roughness usually shows different surface composition as shown in Table 2. The concentration of Sn<sup>4+</sup> dopants of the near ITO surface can be effectively reduced by O<sub>2</sub> plasma treatment. The movement of the surface Fermi level toward the valence band maximum by physical treatment effectively increases ITO work function as shown in Figure 10. By replacing In<sup>3+</sup> atoms with Sn<sup>4+</sup> dopants, thereby
introducing additional positive charge in the near-surface region can present more O dimers on the surface.

The surface chemistry of ITO electrode is complex due to the inherent heterogeneity of these films. The elucidation of the relationship between the electron transfer reactivity of ITO electrode and its microstructure, surface composition is complicated because the surface properties of these films strongly depend on the deposition process and parameters used. The performance of ITO electrode and its electron transfer reactivity strongly depends on its electronic density of states and surface functional groups, whereas sometimes, impurities also determine the performance.

Deposition process and parameters play important role in the structure and properties of ITO films and it is a complicated study due to the inherent heterogeneity of these films. The electron density of states and surface functional groups affects the electron-transfer reactivity of ITO electrodes.

### 3.3. Surface potential and work function

The potential due to the energy differences between bulk and the surface of the film can be defined as surface potential. KFM is a technique by which the surface potential can be measured with detailed analysis at different region on the interface. The changes of the electric surface potential on which the standard explanation of the sensor function is based due to adsorption/desorption can be done by the increase in surface coverage with negatively charged oxygen species. Comparing with other semiconducting oxides, the diffusivity of oxygen in ITO is higher because of particular crystal structure (bixbyite).

Several studies reported that the relationship between surface chemical composition of ITO film (In:Sn:O) and its different properties (Khan, Nakanishi, Kuroiwa, Hoshi, & Osaka, 2011; Mason et al., 1999; Sugiyama, Ishii, Ouchi, & Seki, 2000) to affect the electrochemical properties of the device. Physical treatment is one of the method to control the surface work function of the electrode (Lee, Jang, Kim, Tak, & Lee, 2004; You, Dong, & Fang, 2004). Oxygen plasma treatment is one of them and

#### Table 2. Values of In:Sn evaluated from AR-XPS, AES, and ICP-MS results of samples A, B, and C (Khan et al., 2011)

| Measurement | Sample A | Sample B | Sample C |
|-------------|----------|----------|----------|
| AR-XPS 0°   | 94.6     | 88.12    | 87.13    |
| AR-XPS 40°  | 94.6     | 87.13    | 88.12    |
| AR-XPS 80°  | 94.6     | 83.17    | 83.17    |
| AES         | 88.12    | 81.19    | 80.20    |
| ICP-MS      | 91.9     | 92.8     | 92.8     |

Figure 10. The work function increase in ITO by composition decrease in In, Sn (Jee et al., 2006).
is an effective method to increase the surface work function. Introduction of negative end on the surface by the formation of dipole layer using organics can increase ITO work function as reported by many researchers (Bruening, Moons, Cahen, & Shanzer, 1995; Bruening et al., 1994; Carrara, Nüesch, & Zuppiroli, 2001; Krüger, Bach, & Grätzel, 2000; Zehner, Parsons, Hsung, & Sita, 1999) as shown in Figure 11. Work function is known to be influenced by the electrostatic condition of the surface and usually controlled by using SAM (Jee et al., 2006).

The concentration of ITO surface states is very high due to the degenerate doping that lead to significant change of the electrostatic potential. As a manifestation of the physical part of the depletion layer, the surface Sn concentration found to be depended on the surface Fermi level position. Using photoelectron spectroscopy (PES), or KFM, the direct assessment of the Fermi level position is possible that can be used for straightforward determination of surface potential with respect to the valence band maximum as shown in Figure 12.

The difference between the electrochemical potential and the electrostatic potential of the metal's inside and outside, respectively, is termed as work function (WF) of that metal. The WF can be easily determined by KFM method, considering a fundamental parameter related to electronic structures. Due to the effect on energy barrier height at the heterojunction interface, the work function of ITO has a critical importance as device performance. The introduction of uncertainties due to interfacial layers can deduce the general values of ITO work function range from 4.1 to 5.1 eV. In n-type semiconductor, electrons can be easily excited into the conduction band by the addition of donor impurities contributes electron energy levels high. Whereas in p-type semiconductor, the addition of acceptor impurities contributes hole levels low in the semiconductor band gap, thereby leaving mobile holes in the valence band.
Due to interfacial layers and the uncertainties that creates all these work function values can be deduced from the tunneling characteristics of the electrode heterojunctions. To increase the ITO work function, introduction of negative end dipole organized furthest from the surface is always effective. Many researchers have used organic to introduce surface dipoles for increasing work function as shown in Figure 13.

Since substantial variations of the energy required removing an electron from the Fermi level, the work function is an extremely sensitive indicator. The ultraviolet photoelectron spectroscopy (UPS) measures the lowest work function patch of the surface, whereas KFM method measures the average work function difference under the probe. Therefore, the higher work function values can be obtained by KFM method. The electrostatic condition of ITO surface can change the work function; therefore, surface modification is usually done to increase the work function. Both plasma treatments and acid etching are used in this purpose. Several researchers reported about the SAMs modification to control the surface work function of ITO electrode. As reported by M.Z.H. Khan et al., successive modification with DSS can effectively increase ITO work function as shown in Figure 14.

During doping process, oxygen vacancies can create which plays important role in ultimate work function value determination. The surface morphology and crystallinity of ITO can affect by tin (Sn) that creates many amorphous domains during its addition. Moreover, introducing In and Sn impurities near the surface can easily lower the work function of ITO electrode by altering its surface chemistry.

It is well established that surface treatment of ITO electrode can affect its work function and surface potential. Not only to remove impurities, but also to change the surface chemical composition, surface treatment plays important role. To control the surface chemical composition and surface height distribution, chemical treatment is a very common method.
3.4. Concluding remarks

The effect of surface modification of ITO electrode on its response as sensing device was investigated by various researchers in the last few decades. Several types of polycrystalline ITO electrodes have been studied by employing experimental methods of surface characterization to investigate the effect of surface morphology and composition on its potential response in electrolyte solution. It was revealed that the surface roughness of ITO electrode has a strong effect on its potential stability in electrolyte. From an extensive investigation on the roughness parameters of different types of ITO electrodes, it was observed that in addition to the average roughness and root mean square roughness values, a combination of skewness and kurtosis values is useful for considering the utility of ITO electrode. An electrode with spiky surface often shows an unstable rest potential even at modified state. A slight difference in In:Sn ratio at the near surface of the ITO substrates is remarkable, and consideration to relate with surface roughness. It was observed that a surface with Gaussian like distribution is desired for effective monolayer modification as well as stable rest potential. The difference in the magnitude of the change in work function after monolayer modification among samples was accounted for by the difference in the degree of orientation and coverage of surface-attached molecules.

Funding
The author received no direct funding for this research.

Author details
Md. Zaved Hossain Khan1
E-mail: zaved.khan@yahoo.com

1 Department of Chemical Engineering, Jessore University of Science and Technology, Jessore 7408, Bangladesh.

Citation information
Cite this article as: Effect of ITO surface properties on its potential stability in electrolyte. From chiral counterions to twisted membranes. Journal of the American Chemical Society, 124, 13486–13494. http://dx.doi.org/10.1021/ja027660j

References
Aboul-Enein, H. Y., & Wainer, I. W. (1997).

Source: Author.

Cover image

1170097.

Cogent Engineering (2016), 3: 1170097.

Md. Zaved Hossain Khan,

SAM modification: A review toward biosensor application,

http://dx.doi.org/10.1080/23311916.2016.1170097

Effect of ITO surface properties on its potential stability in electrolyte. From chiral counterions to twisted membranes. Journal of the American Chemical Society, 124, 13486–13494. http://dx.doi.org/10.1021/ja027660j

Bourlangue, A., Payne, D. J., Egdell, R. G., Foord, J. S., Edwards, P. R., Jones, M. O., ... Hutchison, J. L. (2008). Growth of In$_2$O$_3$(100) on Y-stabilized ZrO$_2$(100) by O-plasma assisted molecular beam epitaxy. Applied Physics Letters, 92, 092117. http://dx.doi.org/10.1063/1.2889500

Bruening, M., Moons, E., Cohen, D., & Shanzer, A. (1995). Controlling the work function of CdSe by chemisorption of benzoic acid derivatives and chemical etching. The Journal of Physical Chemistry, 99, 8368–8373. http://dx.doi.org/10.1021/jp9910002e029

Bruening, M., Moons, E., Yaron-Marcovich, D., Cohen, D., Libman, J., & Shanzer, A. (1994). Polar ligand adsorption controls semiconductor surface potentials. Journal of the American Chemical Society, 116, 2972–2977. http://dx.doi.org/10.1021/ja940086c

Brumbach, M., Veneman, P. A., Marrick, F. S., Schulmeyer, T., Simmonds, A., Xia, W., ... Armstrong, N. R. (2007). Surface composition and electrical and electrochemical properties of freshly deposited and acid-etched indium tin oxide electrodes. Langmuir, 23, 11089–11099. http://dx.doi.org/10.1021/la071754u

Buck, R. P. (1978). Ion selective electrodes in analytical chemistry. In H. Freiser (Ed.), Theory and principles of membrane electrodes (Vol. 1, pp. 1–141). New York, NY: Plenum Press.

Budnikov, G. K., Evtugin, G. A., Budnikova, Y. G., & Al’fonsov, V. A. (2008). Chemically modified electrodes with amperometric response in enantioselective analysis. Journal of Analytical Chemistry, 63, 2–12. http://dx.doi.org/10.1134/S1061934808010024

Carrao, M., Müesch, F., & Zuppilui, L. (2001). Carboxylic acid anchoring groups for the construction of self-assembled monolayers on organic device electrodes. Synthetic Metals, 121, 1633–1634. http://dx.doi.org/10.1016/S0379-6779(00)00728-1

Chopra, K. L., Major, S., & Pandya, D. K. (1983). Transparent conductors—A status review. Thin Solid Films, 102, 1–46. http://dx.doi.org/10.1016/0040-6098(83)90256-0

Corry, B., Uilk, J., & Crawley, C. (2003). Probing direct binding affinity in electrochemical antibody-based sensors. Analytica Chimica Acta, 496, 103–116. http://dx.doi.org/10.1016/j.aca.2003.01.001

Dulub, O., Diebold, U., & Kresse, G. (2003). Novel stabilization mechanism on polar surfaces: ZnO(0001)-Zn. Physical
Review Letters, 90, 016102.  
http://dx.doi.org/10.1103/PhysRevLett.90.016102

Durst, R. A., Baumer, A. J., Murray, R. W., Buck, R. P., & Andreieux, C. P. (1997). Chemically modified electrodes: Recommended terminology and definitions. Pure and Applied Chemistry, 69, 1317–1323.

Fang, A. P., Ng, H. T., & Li, S. F. Y. (2003). A high-performance glucose biosensor based on monomolecular layer of glucose oxidase covalently immobilised on indium-tin oxide surface. Biosensors and Bioelectronics, 19, 43–49.

Ferreira, M., Fiorito, P. A., Oliveira, O. N., & Córdoba de Torres, S. J. C. (2004). Enzyme-mediated amperometric biosensors prepared with the Layer-by-Layer (LbL) adsorption technique. Biosensors and Bioelectronics, 19, 1611–1615.

Gardner, T. J., Frisbie, C. D., & Wrighton, M. S. (1995). Systems for orthogonal self-assembly of electroactive monolayers on Au and ITO: An approach to molecular electronics. Journal of the American Chemical Society, 117, 6927–6933.  
http://dx.doi.org/10.1021/ja0031001

Golovanov, V., Maki-Jaskari, M. A., Rantala, T. T., Korotcenkov, G., Brinzari, V., Cornet, A., & Morante, J. (2003). Experimental and theoretical studies of indium oxide gas sensors fabricated by spray pyrolysis. Sensors and Actuators B, 106, 563–571.

Goniakowski, J., Finocchi, F., & Noguera, C. (2008). Polarity of oxide surfaces and nanostructures. Reports on Progress in Physics, 71, 016501.  
http://dx.doi.org/10.1088/0034-4885/71/1/016501

Grishaber, D., Mackenzie, R., Vörös, J., & Reimhult, E. (2008). Electrochemical biosensors - sensor principles and architectures. Sensors, 8, 1400–1458.  
http://dx.doi.org/10.3390/s8031400

Hayashi, K., Iwasaki, Y., Horiuchi, T., Sunagawa, K., & Tate, A. (2005). Selective detection of a catecholamine against electroactive interferents using an interdigitated heteroarray electrode consisting of a metal oxide electrode and a metal band electrode. Analytical Chemistry, 77, 5236–5242.

http://dx.doi.org/10.1021/ac050216p

Horváth, V., Takács, T., Horvá, G., Husztyh, P., Bradshaw, J. S., & Izatt, R. M. (1997). Enantiomer-selectivity of ion-selective electrodes based on a chiral crown-ether ionophore. Analytical Letters, 30, 1591–1609.

http://dx.doi.org/10.1080/00032719708001680

Izake, E. L. (2007). Chiral discrimination and enantioselective analysis of drugs: An overview. Journal of Pharmaceutical Sciences, 96, 1659–1676.  
http://dx.doi.org/10.1021/ps0702802

Jee, S. H., Kim, S. H., Ko, J. H., & Yoon, Y. S. (2006). Study on work function change of ITO modified by using a self-assembled monolayer for organic based devices. Journal of Korean Physical Society, 49, 2034–2039.

Junxiang, H., Sato, H., Umemura, Y., & Yamagishi, A. (2005). Sensing of molecular chirality on an electrode modified with a clay–metal complex hybrid film. The Journal of Physical Chemistry B, 109, 467–4683.

http://dx.doi.org/10.1021/jp0451086

Justin Gooding, J., Meems, F., Yang, W., & Lu, J. (2003). Self-assembled monolayers into the 21st century: Recent advances and applications. Electroanalysis, 15, 81–96.  
http://dx.doi.org/10.1002/elan.200390017

Khan, M. Z. H., Nakanishi, T., & Osako, T. (2011). Potentiometric detection of serotonin, melatonin, and their precursors/ metabolites with monolayer-modified indium tin oxide electrode and their concentration dependency. Sensor Letters, 9, 1849–1852.

http://dx.doi.org/10.1166/sl.2011.1739

Khan, M. Z. H., Nakanishi, T., Kuriow, S., Hoshi, Y., & Osako, T. (2011). Effect of surface roughness and surface modification of indium tin oxide electrode on its potential response to tryptophan. Electrochemistry Acta, 56, 8557–8561.

http://dx.doi.org/10.1016/j.electacta.2011.07.068

Kim, D. C., & Kang, D. J. (2008). Molecular recognition and specific interactions for biosensing applications. Sensors, 8, 6605–6641.

http://dx.doi.org/10.3390/s8106605

Kim, K. B., Tak, Y. H., Han, Y. S., Balk, K. H., Yoon, M. H., & Lee, M. H. (2003). Relationship between surface roughness of indium tin oxide and leakage current of organic light-emitting diode. Japanese Journal of Applied Physics, 42, L438–L440.

http://dx.doi.org/10.1143/JJAP.42.L438

Krüger, J., Bach, U., & Grätzl, M. (2000). Modification of TiO₂ heterostructures with benzoic acid derivatives in hybrid molecular solid-state devices. Advanced Materials, 12, 447–451.  
http://dx.doi.org/10.1002/(ISSN)1521-4095

Lee, K. H., Hong, H. W., Kim, K. B., Tak, Y. H., & Lee, J. L. (2004). Mechanism for the increase of indium-tin-oxide work function by O₂ inductively coupled plasma treatment. Journal of Applied Physics, 95, 586.  
http://dx.doi.org/10.1063/1.1633551

Lin, J., Hu, Q.-S., Xu, M.-H., & Pu, L. (2002). A practical enantioselective fluorescent sensor for mandelic acid. Journal of the American Chemical Society, 124, 2088–2089.  
http://dx.doi.org/10.1021/cr0101971x

Love, J., Estoff, L. A., Kriebel, J. K., Nuzzo, R. G., & Whitesides, G. M. (2005). Self-assembled monolayers of thiocyanates on metals as a form of nanotechnology. Chemical Reviews, 105, 1103–1170.  
http://dx.doi.org/10.1021/cr0300789

Madueno, R., Räsänen, M. T., & Silien, C. (2008). Functionalizing hydrogen-bonded surface networks with self-assembled monolayers. Nature, 454, 618–621.

http://dx.doi.org/10.1038/nature07096

Mason, M. G., Hung, I. S., Tang, C. W., Lee, S. T., Wong, K. W., & Wang, M. (1999). Characterization of treated indium-tin-oxide surfaces used in electroluminescent devices. Journal of Applied Physics, 86, 1688.  
http://dx.doi.org/10.1063/1.370948

Massolini, G., Temporini, C., & Calleri, E. (2008). Penicillin G acylase as chiral selector in LC and CE: Exploring the origins of enantioselectivity. Journal of Chromatography B, 875, 20–29.  
http://dx.doi.org/10.1016/j.jchromb.2008.05.051

Matsuogno, M., Ikeno, T., Nakanishi, T., & Osako, T. (2008). Enantioselective potential response of a human serum albumin-modified ITO electrode for tryptophan. Electrochemistry Communications, 10, 1844–1846.  
http://dx.doi.org/10.1016/j.elecom.2008.09.024

Million, D. J., Hill, I. G., Shen, C., Kahn, A., & Schwartz, J. (2000). Surface oxidation activates indium tin oxide for hole injection. Journal of Applied Physics, 87, 572.  
http://dx.doi.org/10.1063/1.371901

Millot, M. C. (2003). Separation of drug enantiomers by liquid chromatography and capillary electrophoresis, using immobilized proteins as chiral selectors. Journal of Chromatography B, 797, 131–159.  
http://dx.doi.org/10.1016/j.jchromb.2003.08.035

Mizutani, F. (2008). Biosensors utilizing monolayers on electrode surfaces. Sensors and Actuators B: Chemical, 130, 14–20.  
http://dx.doi.org/10.1016/j.snb.2007.07.090

Moore, E., O'Connell, D., & Galvin, P. (2006). Surface characterisation of indium-tin oxide thin electrode films for use as a conducting substrate in DNA sensor development. Thin Solid Films, 515, 2612–2617.  
http://dx.doi.org/10.1016/j.tsf.2006.03.025
Morales, E. H., & Diebold, U. (2009). The structure of the polar Sn-doped indium oxide (001) surface. Applied Physics Letters, 95, 253105. http://dx.doi.org/10.1063/1.3275716

Morales, E. H., He, Y., Vinichenko, M., Delley, B., & Diebold, U. (2008). Surface structure of Sn-doped InO, (111) thin films by STM. New Journal of Physics, 10, 125030.

Moses, P. R., Wier, L., & Murray, R. W. (1975). Chemically modified tin oxide electrode. Analytical Chemistry, 47, 1882–1886. http://dx.doi.org/10.1021/ac00362a043

Mutharasan, A., & Ganesh, V. (2012). Electrochemical characterization of Self-assembled Monolayers (SAMs) of silanes on indium tin oxide (ITO) electrodes – Tuning electron transfer behaviour across electrode–electrolyte interface. Journal of Colloid and Interface Science, 374, 241–249. http://dx.doi.org/10.1016/j.jcis.2012.02.007

Napier, M. E., & Thorp, H. H. (1997). Modification of electrodes with dicarboxylate self-assembled monolayers for attachment and detection of nucleic acids. Langmuir, 13, 6342–6344. http://dx.doi.org/10.1021/la970796o

Niwa, D., Hommo, T., & Osako, T. (2004). Fabrication of organic monolayer modified ion-sensitive field effect transistors with high chemical durability. Japanese Journal of Applied Physics, 43, L105–L107. http://dx.doi.org/10.1143/JJAP.43.1105

Noguero, C. (2000). First principles studies of complex oxide surfaces and interfaces. Journal of Physics: Condensed Matter, 12, R367.

Oh, S. Y., Yun, Y. J., Kim, D. Y., & Han, S. H. (1999). Formation of a Self-assembled monolayer of dianodineocacne and a heteropolycac electrode on the ITO surface. Langmuir, 15, 4690–4692. http://dx.doi.org/10.1021/la9900268

Park, Y., Choong, V., Gao, Y., Hsieh, B. R., & Tang, C. W. (1996). Work function of indium tin oxide transparent conductor measured by photoelectron spectroscopy. Applied Physics Letters, 68, 2699. http://dx.doi.org/10.1063/1.116313

Priolet-Simon, B., Campas, M., & Marty, J. L. (2008). Biomolecule immobilization in biosensor development: Tailored strategies based on affinity interactions. Protein & Peptide Letters, 15, 757–763.

Qiu, H., Yan, J., Sun, X., Liu, J., Coo, W., Yang, X., & Wang, E. (2003). Microchip capillary electrophoresis with integrated indium tin oxide electrode based electrochemiluminescence detector. Analytical Chemistry, 75, 5435–5440. http://dx.doi.org/10.1021/ac034500x

Rasmusson, J. R., Brøms, P., Birgerson, J., Erlendsson, R., & Solanenck, W. R. (1996). The interface surfaces of a CN-substituted poly(phenylethynylene) light-emitting diode, a morphological study. Synthetic Metals, 79, 75–84. http://dx.doi.org/10.1016/0379-6779(96)80134-2

Ross, J. W., Riseman, J. H., & Krueger, J. A. (1973). Potentiometric gas sensing electrodes. Pure and Applied Chemistry, 36, 473–487.

Ruan, C. M., Yang, L. J., & Li, Y. B. (2002). Immunosensor chips for detection of Escherichia coli O157:H7 using electrochemical impedance spectroscopy. Analytical Chemistry, 74, 4814–4820. http://dx.doi.org/10.1021/ac020564b

Schör, T., Schmitz, K., Niemeier, N., Balaban, T. S., Krug, H. F., Schepers, U., & Brä, S. (2007). Solid-phase synthesis, bioconjugation, and toxicology of novel cationic oligopeptides for cellular drug delivery: Bioconjugate Chemistry, 18, 342–354.

Shaya, O., Einati, H., Fishelson, N., Schacham-Diamond, Y., & Rosenwaks, Y. (2010). Transistor gating by polar molecular monolayers. Applied Physics Letters, 97, 053501. http://dx.doi.org/10.1063/1.3476337

Shipway, A. N., Katz, E., & Willner, I. (2000). Nanoparticle arrays on surfaces for electronic, optical, and sensor applications. Chemphyschem: A European Journal of Chemical Physics and Physical Chemistry, 1, 18–52.

Stefan, R. F., von Staden, J. F., & Aboul-Enein, H. Y. (2001). Electrochemical sensors in bioanalysis. New York, NY: Marcel Dekker.

Stout, K. J., Sullivan, P. J., Dong, W. P., Mainsah, E., Luo, N., Mathia, T., & Zahouani, H. (1993). The development of methods for the characterization of roughness in three dimensions (Report EUR 15178 EN). London: Penton Press.

Sugiyama, K., Ishii, H., Ouchi, Y., & Seki, K. (2000). Dependence of indium-tin-oxide work function on surface cleaning method as studied by ultraviolet and x-ray photoemission spectroscopies. Journal of Applied Physics, 87, 295. http://dx.doi.org/10.1063/1.371859

Sun, X. H., & Gillis, K. D. (2006). On-chip amperometric measurement of quanl catecholamine release using transparent indium tin oxide electrodes. Analytical Chemistry, 78, 2521–2525. http://dx.doi.org/10.1021/ac052037d

Theobald, J. A., Oxtoby, N. S., Phillips, M. A., Champness, N. R., & Beton, P. H. (2003). Controlling molecular deposition and layer structure with supramolecular surface assemblies. Nature, 424, 1029–1031. http://dx.doi.org/10.1038/nature01915

Thevenot, D. R., Buck, R. P., Cammann, K., Durst, R. A., Toth, R. A., & Wilson, G. S. (1999). Electrochemical biosensors: Proposed definitions and classification (IUPAC Report). Transactions, vol. 1, 374, 4814–4820.

Tiwari, A., Aryal, S., Pillai, S., & Gong, S. (2005). An amperometric urea biosensor based on covalently immobilized urease on an electrode made of hyperbranched polyester functionalized gold nanoparticles. Talanta, 78, 1401–1407. http://dx.doi.org/10.1016/j.talanta.2009.02.018

Tominaga, M., Kumagai, T., Takita, S., & Toniguchi, I. (1999). Effect of surface hydrophilicity of an indium oxide electrode on direct electron transfer of myoglobin. Chemistry Letters, 15, 1771–1774. http://dx.doi.org/10.1246/cl.1999.769

Trojanowicz, M., & Wcisło, M. (2005). Electrochemical and piezoelectric enantioselective sensors and biosensors. Analytical Letters, 38, 523–547. http://dx.doi.org/10.1081AL-200050157

Vilan, A., Shanzur, A., & Cohen, D. (2000). Molecular control over Au/GaAs diodes. Nature, 404, 166–168. http://dx.doi.org/10.1038/35004539

Wackerbarth, H., Zhang, J., Grubb, M., Hansen, A. G., Ooi, B. L., Christensen, H. E. M., & Ulstrup, J. (2005). Electrochemistry of nucleic acids and proteins – Towards electrochemical sensors for genomics and proteomics. Perspectives in Analytical Chemistry, 1, 485–516. http://dx.doi.org/10.1006/sica.2004.0155

Walker, A., & Catlow, C. R. A. (2010). Structure, stability and work functions of the low index surfaces of pure indium oxide and Sn-doped indium oxide (ITO) from density functional theory. Journal of Materials Chemistry, 20, 10438. http://dx.doi.org/10.1039/c0jm01816c

Willner, I., Lapidot, N., Riklin, A., Kasher, R., & Zohovy, E. (1996). Electron-transfer communication in glutathione reductase assemblies: Electrocatalytic, photocatalytic, and catalytic systems for the reduction of oxidized glutathione. Journal of the American Chemical Society, 118, 1428–1441. http://dx.doi.org/10.1021/ja950191e

Yasaka, T., Yamamoto, T., Kimura, K., & Shono, T. (1980). Simple evaluation of enantiomer-selectivity of crown ether using membrane electrode. Chemistry Letters, 19, 769–772. http://dx.doi.org/10.1246/cl.1980.769

You, Z. Z., Dong, J. Y., & Fang, S. D. (2004). Surface modification of indium-tin-oxide anode by oxygen plasma for organic
electroluminescent devices. Physica Status Solidi (A), 201, 3221–3227. 
http://dx.doi.org/10.1002/PHOS.1521-396X
Zehner, R. W., Parsons, B. F., Hsung, R. P., & Sita, L. R. (1999). Tuning the work function of gold with self-assembled monolayers derived from X−-[C₆H₄−C−C−…C−H₄−SH (n = 0, 1, 2; X = H, F, CH₃, CF₃, and OCH₃)]. Langmuir, 15, 1121–1127. 
http://dx.doi.org/10.1021/la981114f
Zhan, W., Alvarez, J., & Crooks, R. M. (2002). Electrochemical sensing in microfluidic systems using electrogenerated chemiluminescence as a photonic reporter of redox reactions. Journal of the American Chemical Society, 124, 13265–13270. 
http://dx.doi.org/10.1021/ja020907s
Zhang, J., Au, K. H., Zhu, Z. Q., & O’Shea, S. O. (2004). Sol–gel preparation of poly(ethylene glycol) doped indium tin oxide thin films for sensing applications. Optical Materials, 26, 47–55. http://dx.doi.org/10.1016/j.optmat.2004.01.018
Zhang, J. D., Kambayashi, M., & Oyama, M. (2005). Seed mediated growth of gold nanoparticles on indium tin oxide electrodes: Electrochemical characterization and evaluation. Electroanalysis, 17, 408–416. 
http://dx.doi.org/10.1002/10.1016/j.electrochem.2005.01.018
Zheng, D., Wang, N., Wang, F. Q., Dong, D., Li, Y. G., Yang, X. Q., … Cheng, J. (2004). Sensitive chemically amplified electrochemical detection of ruthenium tris-(2,2’-bipyridine) on tin-doped indium oxide electrode. Analytica Chimica Acta, 508, 225–231. 
http://dx.doi.org/10.1016/j.aca.2003.12.002
Zhou, C. G., Li, J. Y., Chen, S., Wu, J. P., Heier, K. R., & Cheng, H. S. (2008). First-principles study on water and oxygen adsorption on surfaces of indium oxide and indium tin oxide nanoparticles. The Journal of Physical Chemistry C, 112, 14015–14020. http://dx.doi.org/10.1021/jp801229g
Zhou, Y., Nagoaka, T., Yu, B., & Levon, K. (2009). Chiral ligand exchange potentiometric aspartic acid sensors with polysiloxane films containing a chiral ligand N-carbobenzoxy-aspartic acid. Analytical Chemistry, 81, 1888–1892. 
http://dx.doi.org/10.1021/ac801751n