Improved Template Surface Treatment

Templates for the active gap tool are similar to those used for Step and Flash Imprint Lithography (SFIL) in dimension and composition. Pillar formation requires templates coated with a conductive film to form the upper electrode. Indium tin oxide (ITO) is commonly utilized because it is both transparent and conductive. ITO films on quartz are also ideal for producing SFIL templates. A new surface treatment method was developed to improve the release properties at the ITO electrode – pillar interface (or ITO – etch barrier interface in the case of SFIL) by binding a fluorosilane to the ITO surface. Conventional silanization methods, based on SiO_2 silanization, are non-robust when applied to ITO. The silane chemistry was optimized to produce a durably bonded functionality by pretreating the ITO surface with base. In comparison to the conventional method, the base pretreatment method results in a surface exhibiting a two-fold increase in the area concentration of fluorine and much improved durability against peel tests and sonication. Since the surface treatment is intended for multi-contact applications, the durability of the fluorinated ITO surface was characterized before and after mechanically and chemically stressing the surface.

9.1 INTRODUCTION

Indium tin oxide (ITO) films exhibit a remarkable combination of properties: high transmittance in the visible spectral region, high reflectance in the IR region, and nearly metallic conductivity - properties that make ITO a functional film in a wide range of commercial applications such as solar cells, flat and touch panel displays, low emissivity windows, and electrochromic devices. A number of new applications have emerged that either require, or benefit considerably from, the ability to introduce non-native atoms or molecules to the ITO surface. For example, ITO has been used as a substrate for various biological sensing technologies[1-6] and has been employed in optoelectronic devices such as organic light emitting diodes (OLEDS).[7-9] ITO has also been used in templates for nanoimprint lithography (SFIL among these)[10, 11]. ITO is ideal for Step and Flash Imprint Lithography (SFIL) for several reasons: (1) The conductive nature of the ITO effectively dissipates electrons during the template e-beam writing process, (2) ITO serves as an effective etch stop during the template fabrication process, (3) The conductive ITO allows for the completed template to be inspected by scanning electron microscopy, a critical step for detecting defects. (4) ITO is transparent, a requirement to photocure the imprinted material.

ITO is also an ideal electrode material for electrohydrodynamic patterning.[12] The transparency of ITO is critical for the function of the white light interferometer used to measure the capacitor gap and for the transmission of UV light during the irradiation step used to cure the pillars. The conductivity is critical for applying the electric field that induces pillar formation. A thin layer of chromium also works as an electrode, but this severely reduces the transparency of the template, as shown in Figure 9.1.

2

25 nm ITO

Transmittance vs Wavelength

6 nm Chromium
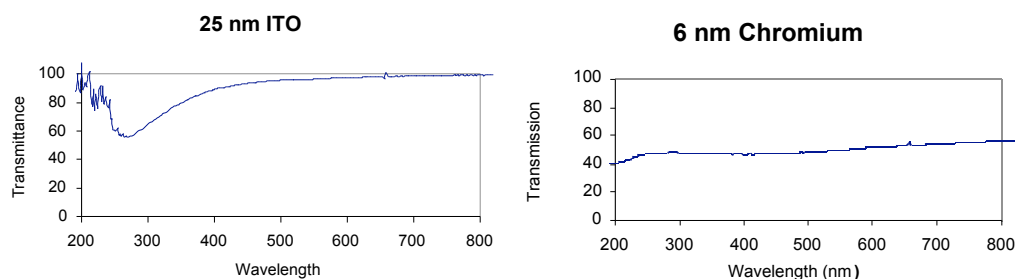
Transmission vs Wavelength (nm)

Figure 9.1: Comparison of the transparency of an ITO film compared to a thin chromium film. ITO is ideal for pillar formation because it is robust, highly conductive, and transparent.

Both SFIL and pillar formation are contact applications, in which the template comes into direct contact with a photocurable fluid. Ideally, upon completion of curing, the template should release cleanly from the cured polymer, as shown in Figure 9.2. The clean release is facilitated by surface treating the template with a fluorinated mono-layer, which lowers the surface energy of the template. The longevity and functionality of the ITO depends on the stability of the treated surface. The primary aim of this work was to develop an ITO surface treatment method that results in a robust monolayer of covalently bound material based on optimized silanization chemistry.
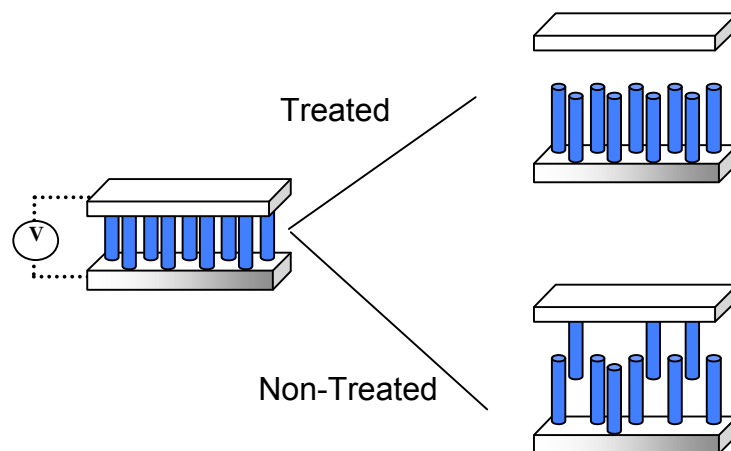
3

Figure 9.2: Treated templates (i.e. upper electrode) cleanly release the pillars upon separation. Pillars adhere to non-treated templates, resulting in defect formation.

Similar to SiO_2, the ITO surface is covered with hydroxyl moieties. Consequently, many of the approaches in the literature for surface treating ITO are identical to methods for treating SiO_2.[1-9, 13, 14] The conventional mechanism is depicted in Figure 9.3, in which the silane reagent undergoes nucelophilic attack by a surface hydroxyl group. The silane illustrated in Figure 9.3 has a fluorinated tail, identical to the silane used in this work to improve the release properties of the ITO surface. However, the approach in Figure 9.3 could be used to attach nearly any functionality to any hydroxyl covered surface. When using these silanization methods, special care must be taken to account for differences between ITO and SiO_2. For example, chlorosilanes must be run in dry conditions due to the HCl etch sensitivity of ITO.[15]

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$C_{10}H_4F_{17}$

R—Si—R
   Cl

OH
              $\longrightarrow$

$C_{10}H_4F_{17}$
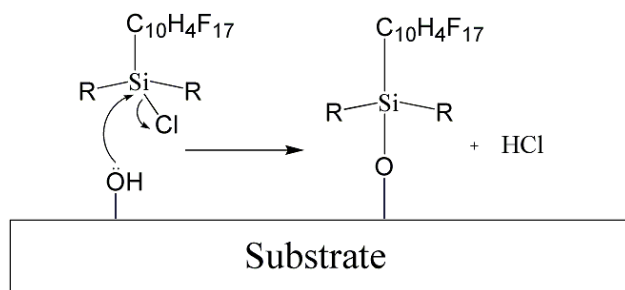
R—Si—R
   O
              + HCl

Substrate

Figure 9.3: Conventional mechanism for surface silylation reaction.

Although silanization is a commonly used approach to modify the surface of ITO, few studies have been performed to study the durability of the ITO treatment. A vapor phase silanization reaction was shown to produce a fluorinated self-assembled monolayer (FSAM) on an ITO SFIL template, which resulted in catastrophic release failure during imprinting.[11] This result is indicative of the limited durability of the FSAM on the ITO surface. FSAM was also formed on ITO by exposing it to an aqueous solution of tridecafluoroctyltriethoxysilane.[12] X-ray photoelectron spectroscopy (XPS) measurements showed that the fluorine level deceased dramatically after ultrasonic bathing in water, propanol, acetone and mechanical rubbing. This fluorine depletion is also indicative of weak bonding of the FSAM on the ITO surface.

Conventional SiO_2 based methods are sufficient for some ITO applications, but in general, none of the existing methods exhibit the durability necessary for repeated contact-type applications. The lack of durability implies that the silane is not covalently bound to the ITO. The ITO surface is less nucleophilic than that of SiO_2,[14-16] resulting in less substitution on the surface and reduced durability. This observation prompted an investigation into ways to improve the durability of silanization methods on ITO.

The approach discussed here involves enhancing established S_N2 chemistry used in the surface modification of SiO_2.[16-19] The reaction can be optimized by utilizing a good leaving group on the silane, increasing the nucleophilicity of the ITO hydroxyl groups, or both.[20] The simplest method is to increase ITO hydroxyl nucleophilicity via deprotonation. Thus, our method relies on a pretreatment of the ITO surface with base, not for the purpose of removing carbonaceous contamination[21] or catalyst formation,[16] but for deprotonation.

Here, base pretreatment is shown to be an effective, yet simple method for dramatically improving the durability of the ITO silanization process. A fluorinated silane is utilized in this study to lower the surface energy of the ITO. After treatment, the quality of the surface treatment is characterized both before and after stressing the surface as a means to quantify the durability of the fluorinated treatment. The durability of the base pretreatment method is compared to conventional silanization methods, in which base pretreatment is not used.

9.2 METHODS AND MATERIALS

9.2.1 Materials

All tests were done on 1_3 in ITO slides (Delta Technology, Stillwater, MN; Part No. CG-61IN-S115). Toluene and tetrahydrofuran (THF) were used separately as solvents for the silanization reactions. The primary base investigated was potassium tert-butoxide. A tri-chlorosilane, (heptadecafluoro-1,1,2,2-tetrahydrodecyl)trichlorosilane (Gelest SIH 5841.0), was used as the surface treatment agent. Tri-chlorosilane was chosen because of its ability to form a covalent network across the surface.[22]

9.2.3 Silanization

The ITO samples were cleaned by sonicating for 30 minutes, first in acetone then in isopropyl alcohol (IPA). The samples were then placed in UV-ozone (UVO-Cleaner Model No. 42, Jelight Company, Inc.) to remove any residual organic contamination and to increase hydroxyl moiety concentration by surface oxidation.[23-30] After cleaning, the samples were stored in an evacuated desiccator until use.

The silanization reaction environment must be dry to avoid polymerization of the silane in solution. Thus, dry solvent (less than 20 ppm water by Karl Fisher titration) was added to a flame-dried, nitrogen-purged, custom glass reaction vessel, designed such that the slides were oriented vertically. Base was added to give a ~0.003 M solution and allowed to react with the surface for 20 min before removal by cannulation. Fresh, dry solvent was added prior to injection of the trichlorosilane (0.2 wt. %) and the reaction was allowed to proceed for two hours, at which point a slightly cloudy solution persisted in the vessel. Finally, the samples were rinsed with solvent and annealed at 130° C for 24 hr.

As a basis for comparison, ITO slides were treated using an identical methodology but without base treatment. This non-base method is hereafter referred to as the "conventional method" because it is the standard technique used for treating SiO_2.[1-9, 13, 14]

9.2.3 Characterization

The quality of the surface treatment was characterized by contact angle, X-ray photoelectron spectroscopy (XPS), and 90° peel force measurements. Characterization was done before and after several procedures designed to remove weakly bonded

silylating agent as a measure of the durability of the surface. A summary of the implemented techniques and their purpose is shown in Table 9.1.

Table 9.1: Procedure Purposes

Processing Step	Characterization
1. Post-Treatment (Mechanically Clean, Sonicate)	---
2. Pre-Stress Test	Contact Angle, XPS
3. Stress Test (Peel Test, Sonicate)	Peel Force
4. Post-Stress Test	Contact Angle, XPS

After silanization, the slides were hazy with oligomeric siloxanes adsorbed from the reaction solution, as shown in Figure 9.4. This physi-sorbed material was removed by passing the slides under a stationary cylindrical cleaning apparatus that applied a constant 10 N force to the surface. The cylinder had a 1.125 in radius and was sheathed in an acetone soaked clean room wipe (Vectra Alpha 10 Texwipe). This mechanical mechanism eliminated the possibility of human bias in the cleaning procedure. The samples were then sonicated sequentially in acetone and IPA for 60 min to further clean the surface.

After cleaning, contact angle images were taken using a goniometer (Ramé-Hart 2000) and analyzed with FTA2000 software (First Ten Ångstroms). The chemical composition of the surfaces were analyzed by XPS (PHI 5700 spectrometer, Physical Electronics). Using monochromatic Al K_ X-rays, spectra were taken at a pass energy of 11.75 eV. XPS binding energies were calibrated using pure gold (Au4f), silver (Ag3d) and copper (Cu2p).

Figure 9.4: Photograph of the ITO slides before and after mechanically cleaning. The "post-treatment" sample is hazy with loosely bound material. After cleaning, the "post-clean" sample is transparent.

Peel tests were performed using an Instron 5848 Mircotester, which measures the force necessary to remove a film at a constant velocity normal to the substrate. In addition to removing weakly bonded species, this peel test also provides a qualitative measure of the work of adhesion. To perform the peel test, a pliable clean wipe (Berkshire LabX123 Item #:LB123.090.60) was photopolymerized to the surface using a 1:1 liquid mixture of thiol-ene, pentaerythritol tetrakis(3-mercaptopropionate) (Aldrich) and tris [4-(vinyloxy)butyl] trimellitate (Aldrich). The clean wipe was chosen for its large tensile strength, which maximized the 5 N load cell in tensile mode with no observable strain deformation of the wipe. During each peel test, an average force was measured in the region between 25 to 75% of total extension to eliminate end effects. In all cases, the thiol-ene released from the substrate such that the polymerized thiol-ene remained exclusively on the clean wipe during peeling. Five peel tests were performed on each slide. The peel test concept is illustrated in Figure 9.5.
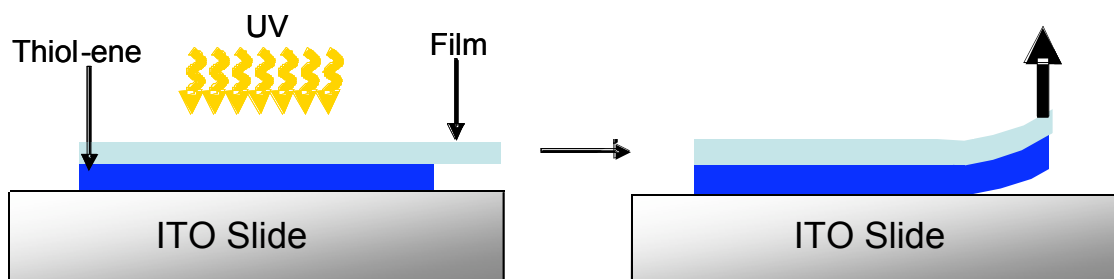
Figure 9.5: Peel test illustration. A photocurable liquid, thiol-ene, is photocured between the ITO and a pliable film. The adhered film is then peeled from the surface while measuring the force.

After completing the peel tests, the samples were cleaned by sonication in acetone and IPA for 60 min and characterized by contact angle and XPS measurements to quantify changes in the surface resulting from the various durability stress tests.

9.3 RESULTS

The key finding of this work is that conventional silanization methods used to treat SiO_2 create non-robust, heterogeneous treatments when applied to ITO. However, the quality of the surface treatment can be dramatically improved through the use of a base pretreatment. This simple method only differs from the conventional method in that the ITO surface is exposed to potassium tert-butoxide prior to the addition of tri-chlorosilane. Table 9.2 provides a comparison of the treatment qualities both before and after durability stress tests (i.e. sonication and peel tests). The values reported in Table 9.2 are averages of over thirty measurements taken on five different samples for each treatment condition. The control sample was exposed to all of the processing equipment and steps as the other samples, but it was not silanized or exposed to base. The control has a larger contact angle than a freshly UV-ozoned sample. This phenomenon has been investigated throughout the literature.[24, 30]

Table 9.2: Summary of Results

Substrate	Contact Angle (Pre-Peel)		Contact Angle (Post-Peel)		Peel Force (N)	
Method (solvent)	Average	St. Dev.	Average	St. Dev.	Average	St. Dev.
Control	59.1	5.6	55.5	4.3	0.368	0.047
Conventional (THF)	67.6	9.6	59.9	2.8	0.167	0.016
Conventional (Toluene)*	83.7	11.4	72.3	12.3	0.109	0.029
Base Treatment (THF)	112.6	2.4	108.0	2.8	0.058	0.007

* The SiO_2 side of the slide gave a contact angle well above 100°

The magnitude of the contact angle measurement is one indication of the quality of the surface treatment. Similarly, the standard deviation of the contact angle provides a measure of the heterogeneity of the surface. As seen in Table 9.2, the base pretreatment method produced larger contact angles with smaller standard deviations at every stage of measurement as compared to the conventional method. The conventional method contact angle dropped significantly after durability stressing to 72°, only slightly better than the control. This drop implies that loosely bound silylating agent was removed during stressing, indicative of a physi-sorbed film. The large contact angle standard deviations of the conventional method are indicative of a non-uniform surface treatment.

In contrast to the conventional method, the use of a base pretreatment created a large initial contact angle that remained large (~110°) after durability stressing. The base

pretreatment method had a significantly lower standard deviation for each set of measurements, indicative of a more homogenous treatment.

Peel tests provide a means to both stress and characterize the surface simultaneously. The measured peel force can not be directly converted to an established metric, such as work of adhesion, but it is indicative of the ease with which the peel releases at the surface. The general behavior of the conventional method compared with the base pretreatment method was consistent with the contact angle data. The average peel force of the conventional method was a factor of two larger than the base treated method, and the force for the conventional method also had a larger standard deviation (both absolute and normalized). Again, this measurement was indicative of a heterogeneous, weakly bonded film.
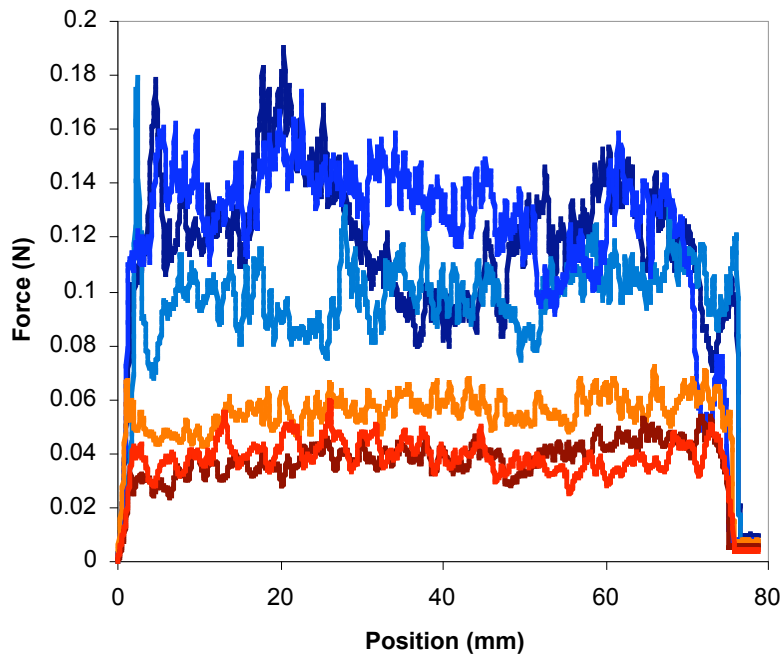
Figure 9.7: Typical peel force plot of the schematic in Figure 9.5. The force required to remove a photo-adhered film from the substrate is measured as a function of displacement. The blue tinted data represents the conventional method and the red tinted data represents the base pretreated method. The base pretreated method has reduced variability, indicative of a uniform treatment.

The notable improvement achieved by base pretreatment could be the result of several factors. Evidence points to base activating the SiO_2 surface hydroxyls, resulting in a more nucleophilic substrate.[31] However, the possibility exists that the base could be playing a catalytic role in the treatment, since amine bases have been used as SiO_2 surface treatment catalysts.[16] None of the bases here were structurally equivalent to the catalysts used previously, due to the insolubility of the pentacoordinate silicon - tertiary amine salt intermediate of the particular silane used. Regardless, the possibility of base catalysis was investigated by a "half-slide" experiment performed such that an ITO slide was only half submersed in potassium tert-butoxide solution. After removing the base, the reaction vessel was filled with chlorosilane solution such that the whole slide was submerged. The bottom, base pretreated half of the slide behaved much like the base pretreated results shown in Table 9.2, with an average contact angle of 104.3° and standard deviation of 1.5°. However, the top half of the slide, which was not directly exposed to base, did not treat as well, indicated by its relatively low contact angle of 82.0° and large standard deviation of 16.3°. This eliminated the possibility of trace amounts of residual base catalyzing the surface reaction. Also, the half of the slide unexposed to base had a much hazier film on the surface than the base treated counter-part, demarcated by a sharp line. This may be indicative of a greater propensity for physi-sorption of oligomers from solution onto a surface that has not been base treated.

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The conventional method slides were consistent with this observation, producing a much hazier film than the base pretreated samples.

System parameters were varied to determine the importance of factors such as solvent, base counter ion, and base strength. Solvent played a significant role in the conventional method, consistent with accepted reaction coordination theory.[16] Compared to toluene, THF is a very poor solvent for the conventional method, as shown in Table 9.2. However, THF proved to be a slightly better solvent for the base pretreatment method (~15° higher contact angle compared to toluene). A possible explanation for this behavior is that the more polar THF solvent provides better solubility of salts formed by the base, outweighing any reaction coordination benefits provided by the toluene. In addition to varying the solvent, two different counter ions for tert-butoxide were investigated. As expected, there was no statistically significant difference between lithium tert-butoxide and potassium tert-butoxide.

The use of stronger bases such as LiHMDS (pKa = 30) and nBuLi (pKa = 50) did not enhance the performance of the surface treatment compared to tert-butoxide (pKa = 18). In some cases, stronger bases actually performed worse than the tert-butoxide, albeit much better than the conventional methods. For example, the LiHMDS gave values of 95° and 85°, before and after peeling. This behavior may be due to increased salt or polymer formation in solution, which could adsorb onto the surface and block reactive sites.

XPS studies complimented the contact angle and peel force measurements. Table 9.3 shows the relative fluorine area concentration compared to indium (i.e. the substrate). The base pretreatment method is clearly superior, both in its initial fluorine surface

concentration and its ability to retain the fluorine after durability stressing. The relative fluorine intensity decreased 40% for the base treated samples, whereas the conventional method decreased 60%. Fluorine decreases in both samples might imply the existence of physi-sorbed polymer regardless of the method. After peeling, the base treated method had an area concentration ~2.5 times larger than the conventional method with a significantly smaller standard deviation, indicative of a more uniform treatment. The untreated ITO control has 0-6 % fluorine, so the conventional method post-peel signal is only slightly larger than the baseline.

Table 9.3: XPS results

Treatment Method	Pre-peel		Post-peel	
	% Fluorine	St. Dev.	% Fluorine	St. Dev.
Conventional	40	14	16	16
Base Pretreatment	70	1	42	4

9.4 DEMONSTRATIONS

The ultimate goal of this study is to reduce template contamination during pillar formation, as shown in Figure 9.2. Thiol-ene pillars were formed on an untreated ITO

template. After one experiment, the template was grossly contaminated with thiol-ene residue, as evident by optical microscopy (Figure 9.8, left image). In contrast, a treated template remains residue free after nine experimental runs of pillar formation (Figure 9.8, right image). The template was treated using the technique described in Sections 9.2-9.3.

In addition to reducing adhesion of the thiol-ene to the template, the treated template also impacts the contact angle of the pillar at the upper electrode. Figure 9.9 is a scanning electron micrograph of a pillar array produced with a freshly treated template. In contrast, Figure 9.10 is a micrograph of a pillar array produced using an untreated template. The untreated template is wetting towards the thiol-ene, whereas the treated template produces a pillar with a larger contact angle. The contact angle is estimated to change from ~60° for the untreated template to ~90° for the treated template.
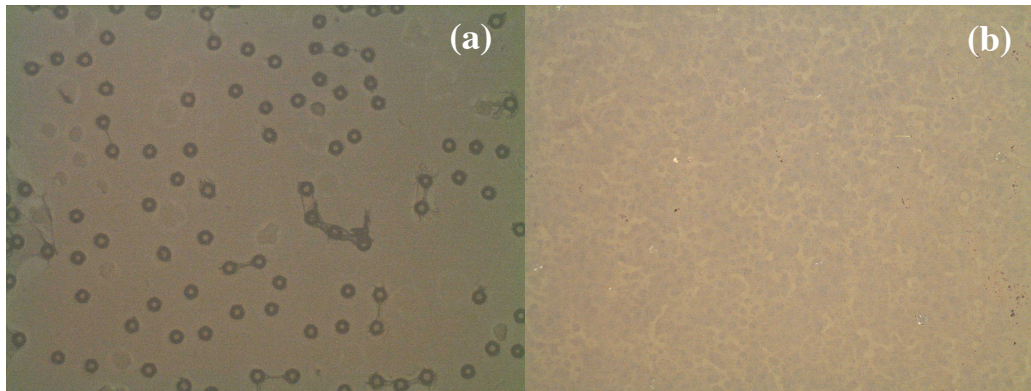

Figure 9.8: Optical micrographs of the ITO template surface at 10x magnification. (a) After one run, the untreated template is grossly contaminated with residue. (b) After nine experiments, the ITO surface remains residue free. Image widths 1170 _m.
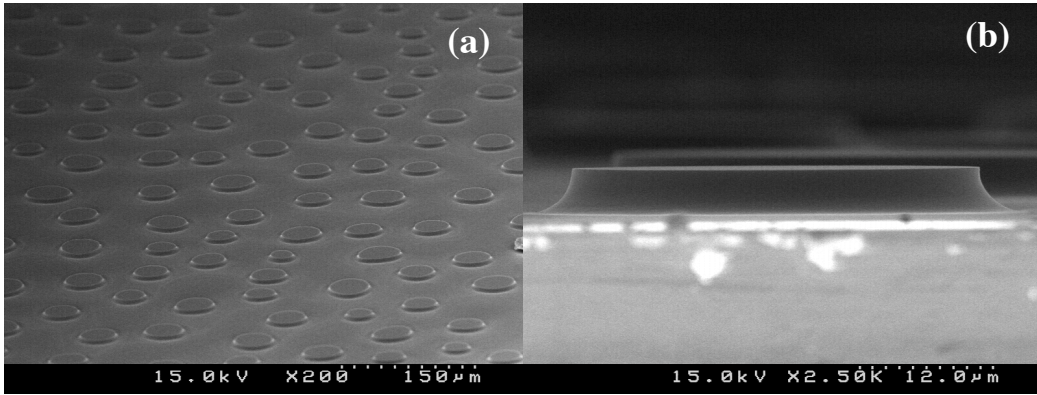
Figure 9.9: Electron micrographs of pillars formed using a surface treated template. (a) Overview (b) A cross section view of a pillar with a non-wetting upper contact angle.
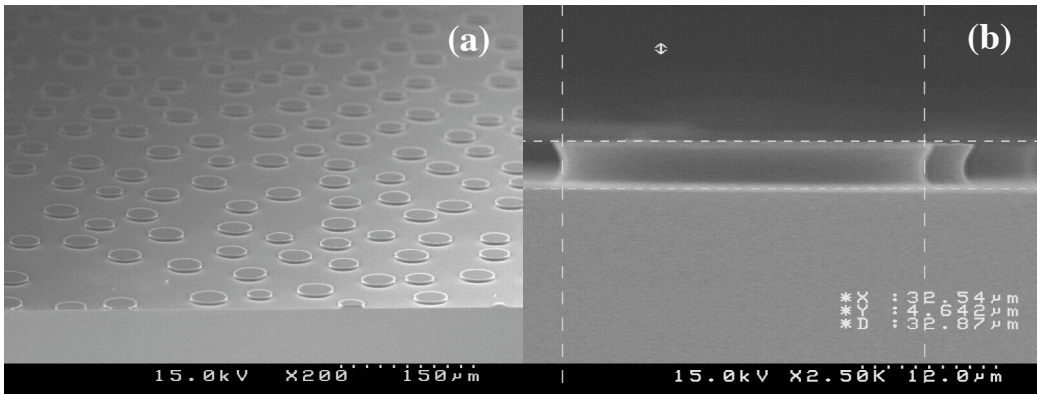

Figure 9.10: Electron micrographs of pillars formed using an untreated template. (a) Overview (b) A cross section view of a pillar with a non-wetting upper contact angle.

9.5 CONCLUSIONS

Base treatment was shown to give both better coverage and a more durable ITO surface treatment than conventional SiO_2 surface treatment methods. The contact angle of the base pretreated ITO was higher than the conventional method, indicative of a better surface treatment. The base pretreated ITO also had a lower contact angle standard

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deviation than the conventional method, indicative of a more uniform surface coverage. XPS data corroborated these findings, showing more fluorine with a smaller standard deviation on the surface of the base treated slides compared to the conventional method. By all metrics utilized, the base pretreatment provided a more durable surface treatment after stressing the surface with controlled mechanical cleaning, sonication, and 90 degree peel tests. The base does not act as a catalyst; rather it appears to be deprotonating the ITO surface, making it more reactive towards the chlorosilane. This ultimately results in more covalent linkages to the substrate that are responsible for improved durability. An ITO treated template was shown to reduce pillar residue and improve the longevity of a template for processing.

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