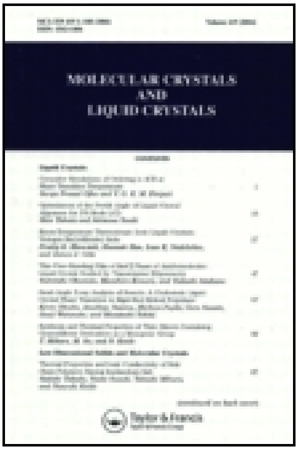

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Structural Effect on Formation of Alkylsilane Self-Assembled Monolayers on Indium Tin Oxide Surface

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Structural Effect on Formation of Alkylsilane Self-Assembled Monolayers on Indium Tin Oxide Surface

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The effects of immersion time and the number of chlorine attached to silane atom on the formation of self-assembled monolayers (SAMs) on indium tin oxide (ITO) surface were examined by scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS), and contact angle measurements. Among octadecyltrichlorosilane (OTS), octadecyldichloromethylsilane (ODDMS), and octadecyldimethylchlorosilane (ODMS), OTS SAMs on ITO surface formed after 1 h deposition at room temperature have a high contact angle value of 86° compared to ODDMS and ODMS SAMs with 45° and 31°, reflecting that OTS on ITO surface would form a high-quality SAMs with a hydrophobic surface. STM imaging revealed that the surface structure of OTS SAMs on ITO surface was markedly different from that of bare ITO surface resulting from the the adsorption of OTS molecules. In addition, XPS measurements showed that the formation of OTS SAMs is strongly driven by the chemical reactions between the Si atoms and the hydroxyl group of ITO surface during self-assembly.

Keywords: alkylsilane; indium tin oxide; scanning tunneling microscopy; self-assembled monolayers

INTRODUCTION

Indium tin oxide (ITO) is transparent and conducting material. It can be used as a transparent conducting oxide for various optoelectronic devices such as solar cells, light-emitting diodes, and optical waveguides [1–10]. The formation of SAMs on ITO surface by phosphonic acids [1,2], carboxylic acids [3–7], thiols [8,9], and amines [10] has been examined by several research groups. It was found that SAMs

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with a high degree of structural order were not formed by those molecules because the headgroups do not bind strongly to ITO surface. On the other hand, there have been a few reports concerning SAM formation of organic silane compounds on ITO surface via silane chemistry under optimized condition [6–9]. The general conclusion of the studies is that the formation of densely packed defect-free SAMs on ITO is difficult due to the high surface roughness and low hydroxyl coverage [10]. However, alkylchlorosilane can bind strongly to the ITO surface under suitable experimental conditions.

To obtain a patterned ITO, alkylsilane SAMs on ITO can be used as excellent photo resist for etching [11]. In addition, strategy to silanize the ITO via silane chemistry is commonly used in biosensor fabrication [5,9–11]. Therefore, it is very important to obtain high-quality alkylsilane SAMs for further various technical applications. In this study, we examined the effects of immersion time and the number of chlorine attached to Si atom on the formation of SAMs on ITO surface, which were mainly characterized by scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS), and contact angle measurements.

EXPERIMENTAL

Octadecyltrichlorosilane (OTS) was purchased from Aldrich and octadecyldichloromethylsilane (ODDMS) and octadecyldimethylchlorosilane (ODMS) were purchased from Tokyo Chemical Industry (Tokyo, Japan) and used without further purification. The ITO sheets were cut into $10 \times 10\,\text{mm}^2$ slide and cleaned by UV/Ozone cleaner for 7.5 minutes. Anhydrous deposition of alkylsilane was performed in a dry glove box filled with nitrogen gas. All alkylsilane toluene solutions were prepared in anhydrous atmosphere below 5% of humidity to avoid polymerization. Alkylsilane SAM samples were prepared by dipping the ITO substrates in solutions of corresponding alkylsilanes for 1 and 4 h. Organic alkylsilane SAM samples on ITO surface were washed with toluene and stored in vacuum packing bags to prevent oxidation and contamination at room temperature prior to use.

STM measurements were performed using NanoScope E (Veeco, Santa Barbara, CA) with a commercial Pt/Ir (80/20) tip. All STM images were obtained using the constant current mode in air at room temperature. XPS measurements were performed using an ESCALAB 250 system (Thermo VG Scientific, UK). A monochromatized AlKα line (10 kV, 150 W) was used as the excitation source (1486.6 eV). Contact angle (CA) measurements were carried out using an automatic contact angle measuring system (model: Easydrop DSA20S, KRÜSS, Germany). Water contact angles were measured at RT on the SAM samples using the sessile drop method. The obtained CA in this study is the average of the contact angles measured at five different positions of sample surfaces.

RESULTS AND DISCUSSION

Figure 1 shows water static contact angles of OTS, ODDMS and ODMS SAMs on ITO surfaces formed after 1 and 4 h immersion of ITO substrates in a 10 mM solution of corresponding alkylsilane compounds at 50°C. The bare ITO water contact angle depends significantly on the pretreatment. We found that the contact angle for pretreated surface by UV/ozone is below 10°, which reflects the hydrophilic surface. Water static contact angles of OTS, ODDMS and ODMS SAMs on ITO surfaces formed after 1 h immersion were measured to be 86°, 45°, and 31°, respectively. OTS SAMs has a higher contact angle value compared to ODDMS and ODMS SAMs, which strongly implies that OTS can form a relatively well-organized SAMs with a methyl group termination, as in the case of alkanethiol SAMs on gold. However, ODDMS and ODMS SAMs have still a very low contact angle value less than ~50°, implying the incomplete SAM formation. On the other hand, after the increase of immersion time

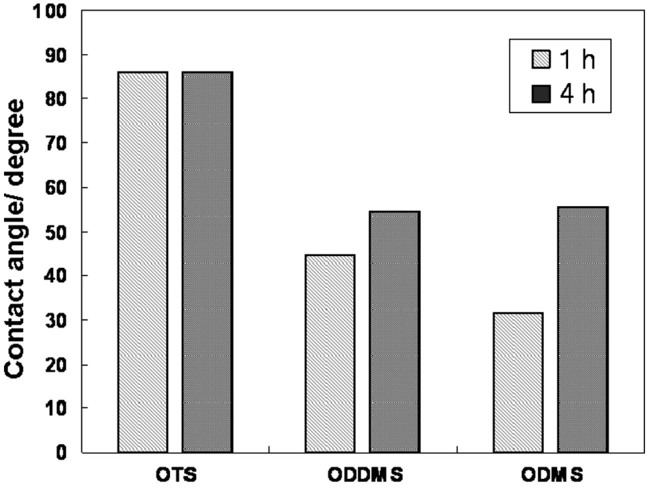

FIGURE 1 Water static contact angles of OTS, ODDMS and ODMS SAMs on ITO surfaces formed after 1 and 4 h immersion of ITO substrates in a 10 mM solution of corresponding alkylsilane compounds at 50°C.

from 1 to 4 h, water static contact angles of OTS, ODDMS and ODMS SAMs on ITO surfaces were measured to be 86°, 54°, and 55°, respectively. We found that the contact angle values for OTS SAMs do not change even if the immersion time increases, whereas those for ODDMS and ODMS SAMs largely increase, suggesting that these molecules still need a time to form SAMs compared to OTS. Based on our results, it is reasonable to consider that SAM formation by alkylsilanes can be strongly influenced by their molecular structures. The active reaction part of Si atom in OTS molecules has three electron-withdrawing chlorine groups. As a result, the Si atoms in OTS can react more easily with ITO surface compared to those in ODDMS and ODMS attached to one or two chlorine groups, resulting in the formation of high structural degree of OTS SAMs. In addition, it can be also considered that one or two methyl groups attached to Si reaction centers of ODDMS and ODMS molecules could hamper surface reaction with ITO surface.

The high roughness of ITO makes it impossible to use ellipsometry to measure the thickness of the films. In addition, atomic force microscope (AFM) images of alkylsilane SAMs on ITO surface do not show any significant structural differences between the bare ITO surface and SAM covered with ITO surface. It is well known that STM is the most powerful means for obtaining molecular-scale information of organic layers on solid surface. In order to understand the structural changes after SAM formation, we examined alkylsilane SAM samples on ITO surface by STM. STM image in Figure 2(a) shows the surface structure of bare ITO surface after UV/ozone cleaning. Figures 2(b), (c), and (d) show the surface structures of alkylsilane SAMs on ITO surface. Although it is hard to obtain molecular-scale features of organic SAMs on ITO surface due to a large roughness of ITO surface, STM image in Figure 2(b) shows that the surface structure of OTS SAMs is markedly different from that of bare ITO surface due to the adsorption of OTS molecules. However, STM images for ODDMS and ODMS SAMs in Figures 2(c) and (d) show a similar surface structure compared to the bare ITO surface. As revealed by contact angle measurements, the contact values for ODDMS and ODMS SAMs are not significantly changed after the adsorption of those molecules on ITO surface compared to OTS SAMs. As a result, we only observed a remarkable structural change from OTS SAMs. We would like note that of ODDMS and ODMS SAMs formed after longer immersion for 4 h have complete different structures compared to the bare ITO surface due to a large amount of adsorption of molecules, which is good consistent with contact angle measurements.

Figure 3 shows XPS spectra of OTS SAMs on ITO surface formed after 1 h immersion of ITO substrates in a 10 mM solution at 50°C.

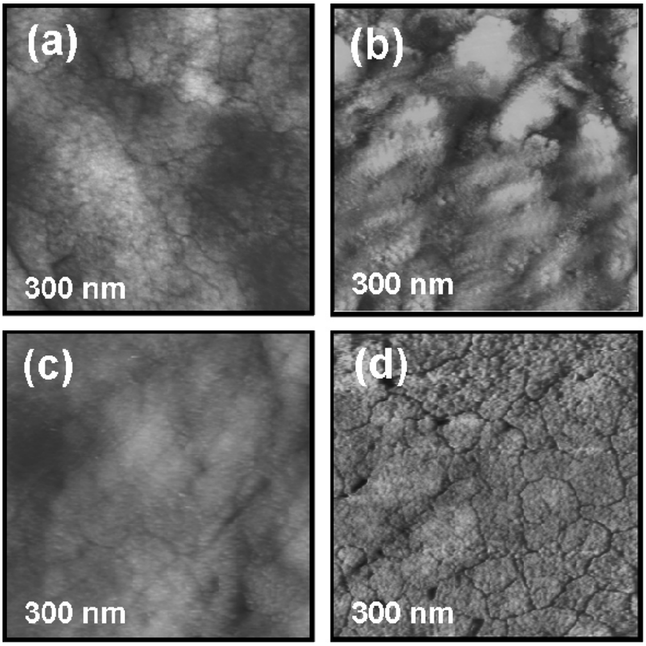

FIGURE 2 STM images showing surface structures of (a) bare ITO, (b) OTS, (c) ODDMS, and (d) ODMS SAMs on ITO formed after immersion of the ITO substrates in a 10 mM solution for 1 h.

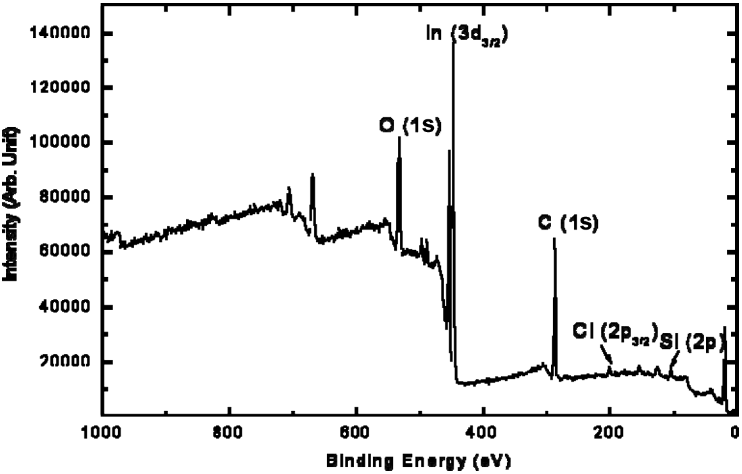

FIGURE 3 XPS spectra of OTS SAMs on ITO surface formed after 1 h immersion of ITO substrates in a 10 mM solution at 50°C.

We clearly observed XPS peak in the Si 2 p region corresponding to the oxidized Si atoms at 103.38 eV, which means that OTS SAMs were formed via chemical reaction between the Si atoms in OTS and surface hydroxyl group of ITO. In the cases of ODDMS and ODMS SAMs, the peak intensities for the oxidized Si 2 p peak is relatively weaker than those for OTS SAMs (data not shown here), as suggested by contact angle measurements.

CONCLUSION

The SAM formation by OTS, ODDMS, and ODMS molecules on ITO surface was examined by STM, XPS, and contact angle measurements. Water static contact angles of OTS, ODDMS and ODMS SAMs on ITO surfaces formed after 1 h immersion were observed to be 86°, 45°, and 31°, respectively. The formation of high structural degree of OTS SAMs can be ascribed to the low electron density property of Si atoms in OTS attached three electron-withdrawing chlorine groups, resulting that the Si atoms can be more effectively react with the hydroxyl oxygen of ITO compared to those in ODDMS and ODMS. STM imaging revealed that the surface structure of OTS SAMs on ITO surface was markedly different from that of bare ITO surface resulting from the the adsorption of OTS molecules. XPS measurements showed that OTS SAMs were formed via chemical reaction between the Si atoms in OTS and surface hydroxyl group of ITO. Our results will be useful in obtaining a high quality and reproducible alkylsilane SAMs on ITO surface.

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