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Electrochemical Investigation of Chemical Lift-off Lithography on Au and ITO

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ABSTRACT

Chemical lift-off lithography (CLL) on Au and indium tin oxide (ITO) were investigated using electrochemical methods in terms of the coverage, stability, and substrate-dependence. Self-assembled monolayers (SAMs) of 11-mercaptoundecanol (MUO) on Au and hydroxyundecylphosphonic acid (HUPA) on ITO were patterned by an oxygen plasma-activated PDMS stamp. Siloxyl groups (Si—OH) from the activated PDMS formed covalent bonds with the hydroxyl groups of the SAM (—OH) on the Au and ITO substrate, which enables the detachment of the SAM molecules from the surface, called CLL. The interfacial properties of the SAM-modified electrodes and post-CLL electrodes were investigated with cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The results revealed that *ca.* 78% of the SAM on Au is detached by CLL and the remaining SAM is stable during subsequent SAM formations. For alkanephosphonic acid on ITO, *ca.* 57% of the SAM was removed in terms of electrochemistry indicating the dependence of CLL on the anchoring groups. AFM images show the pattern formation by CLL on both Au and ITO.

1. Introduction

The fabrication of small features on a large-area by lithography has been key in the modern semiconductor industry and in the research field that makes nanometer-scale structures. Despite state-of-the-art photolithography, several methods including dip-pen lithography [1], electron-beam lithography [2] and soft lithography [3] have been introduced to overcome the limitations of photolithography such as restricted resolutions and time-consuming prototyping. Especially, soft lithography with molecular inks such as alkanethiols has been widely applied to make various chemical patterns over a large area, however, the resolution of the printed molecule is limited due to lateral diffusion and gas-phase deposition. Recently, to overcome the limitation of soft lithography, subtractive patterning of self-assembled monolayers (SAMs) called chemical lift-off lithography (CLL) was introduced [4–6]. In contrast to additive transfer of alkanethiols from stamp to substrate, CLL selectively removes the preformed SAM on Au through covalent bonds between the hydroxyl group at the terminal position of the SAM and the epoxy group of the polydimethylsiloxane (PDMS) stamp activated by O_2-plasma. Thus, the typical drawbacks of microcontact printing such as lateral diffusion and gas-phase deposition can be avoided enabling high resolution features up to 40 nm [4]. Taking advantage of the preformed SAM, CLL was applied to fabricate the source-drain terminals for a field-effect transistor [5]. The chemistry of desorption through the covalent bond also has a significant role in the CLL process. About 80% of hydroxyl-terminated alkanethiols are detached by CLL based on Fourier-transform infrared reflection absorption spectroscopy where the Au—Au bonds within Au are broken more easily than the Au—S bonds [5]. These characters of CLL enables a higher hybridization efficiency by controlled DNA patterning [6]. The post-CLL SAM, however, has not yet been investigated in depth. In particular, the coverage and the stability of the post-CLL SAM would be significant for a displacement reaction. Substrate-dependence is another issue of CLL because only competition between Au—S and Au—Au bond breaking was investigated. Because the SAM can be formed on various substrates including metals and metal oxides through specific chemical interactions between the functional groups of organic molecules and the surface of the substrate, a study of CLL on other substrates with different chemistries is necessary to extend CLL to various applications.

Electrochemistry provides a simple and sensitive method to quantify the adsorbed molecules on an electrode surface.

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Electrochemical reductive desorption is a representative method for precise quantification [7]. The electrochemical impedance technique also provides various information on the SAM from double layer capacitance (C_{dl}) and charge transfer resistance (R_{ct}) estimated based on an appropriate equivalent circuit [8]. Herein, we report the electrochemical investigation of the CLL process in two model systems: 11-Mercaptoundecanol (MUO) on Au and 11-hydroxyundecylphosphonic acid (HUPA) on indium tin oxide (ITO). The latter system could provide general information on the CLL process on metal oxide substrates. The charge transfer of $Fe(CN)_6{}^{3-}$ both on a SAM-modified electrode and on post-CLL electrodes were investigated with cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). EIS was adopted to investigate the SAM of alkyl phosphonic acid on ITO. The coverage of the SAM was estimated based on the two models from the R_{ct} or C_{dl}. In the case of MUO on Au, the remaining coverage of the SAM was also monitored by reductive desorption to confirm which model is more suitable for the quantification of the SAM from the EIS. Displacement of 11-ferrocenyl-1-undecanethiol (FCU) on the post-CLL Au was characterized electrochemically to determine the coverage and stability. The results show that the detached coverage of the preformed SAMs were up to ca. 78% and 57% on Au and ITO, respectively. The residual SAM on the Au after CLL is as stable because it resists displacement with alkanethiols for the subsequent insertion of adsorbate.

2. Experimental

2.1. Materials

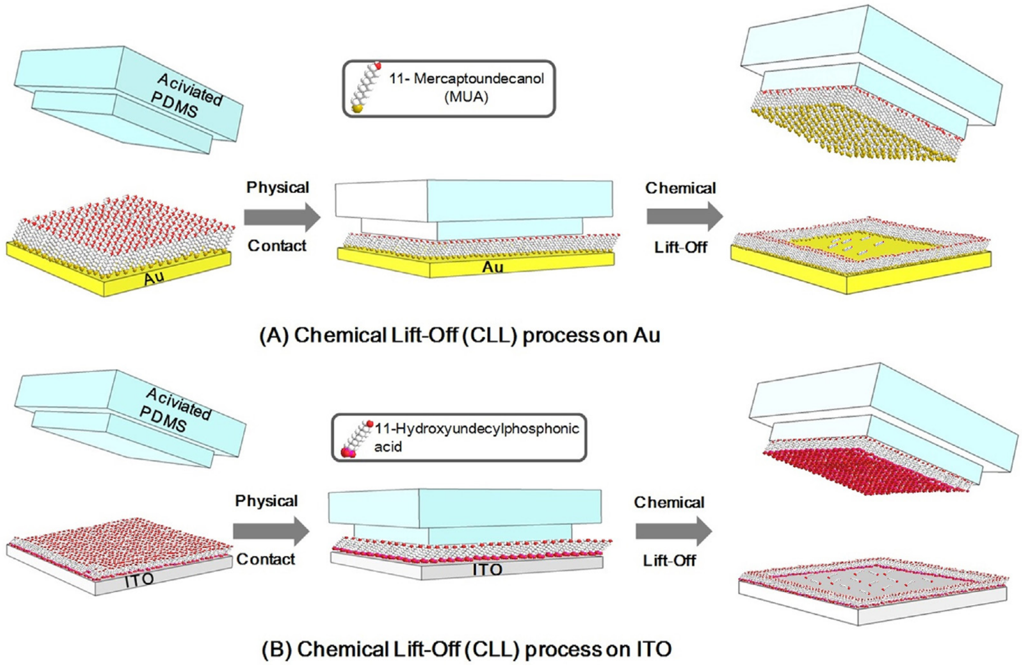
11-Hydroxyundecylphosphonic acid (HUPA, 95%) was purchased from Alfa-aesar. 11-Mercaptoundecanol (MUO, 97%), 11-ferrocenyl-1-undecanethiol (FCU, 95%), potassium ferrocyanide ($K_4Fe(CN)_6$, 100.4%), and perchloric acid ($HClO_4$, 70%) were purchased from Sigma-Aldrich. Potassium hydroxide (KOH, 95%) and Potassium ferricyanide ($K_3Fe(CN)_6$, 98%) were purchased from Samchun chemicals. Potassium nitrate (KNO_3, 99%) was purchased from JUNSEI. All chemicals were used as received, and ultrapure water (resistivity 18.2 $M\Omega \cdot cm$) was produced with a Milli-Q water purification system. All electrochemical cells were cleaned with Nochromix (Godax Lab., Inc.) cleaning solution and rinsed with ultrapure water.

2.2. Preparation of self-assembled monolayers

Gold electrodes were prepared by electron beam evaporation of 4 nm of Ti followed by 200 nm of Au onto Si (100) wafers. The electrode was cleaned for 3 min. in piranha solution (3:7 by volume, 30% H_2O_2:H_2SO_4; *Caution: piranha solution reacts violently with most organic materials and must be handled with extreme care*), rinsed with H_2O and ethanol, and dried under a stream of nitrogen. The cleaned Au was immersed in a 1 mM ethanolic solution of 11-mercaptoundecanol (MUO) overnight. ITO electrodes from Samsung Corning (10 ohm/sq, 185 nm of ITO on a 1.1 cm thick glass by sputtering, Daegu, Korea) were cut into small pieces (1 cm × 2 cm) and cleaned using acetone, isopropyl-alcohol and pure water with 15-min. ultrasonication. The cleaned ITO was immersed in a 1 mM water solution of 11-Hydroxyundecylphosphonic acid (HUPA) overnight. After the formation of the SAMs, the Au and ITO were rinsed with each solvent several times and dried under a stream of nitrogen.

2.3. CLL of self-assembled monolayers

A 10:1 mass ratio of SYLGARD® 184 silicone elastomer base (Dow corning) and curing agent (Dow corning) was mixed roughly. An uncured mixture was poured onto the Si wafer to fabricate the flat PDMS stamp, then degassed under a vacuum, and cured at 65 °C overnight. The PDMS stamp was activated by a 30 s exposure to O_2 plasma (Femto Science Inc.) at a power of 100 W. The activated PDMS stamp was contacted with the SAM-modified substrate for 8 hours. To ensure a conformal contact, vertical pressure was applied to the stamp (1 cm × 1 cm) using a weight (2 Korean coins, 100 won denomination, ca. 5.4 g/coin). For higher vertical pressures (4, 6, and 8 coins), the electrochemical data were very similar to that for 2 coins indicating the negligible effect of pressure on CLL except 8 coins, in which the pressure may induce physical damage on the SAM (see supporting information). As a



Scheme 1. Illustration of the chemical lift-off (CLL) process (A) on Au and (B) on ITO.