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Immobilization of aromatic aldehyde molecules on indium tin oxide surface using acetalization reaction

Tomohiro Nakayama, Toshinori Matsushima, Hideyuki Murata *

School of Materials Science, Japan Advanced Institute of Science and Technology, 1-1 Asahidai, Nomi, Ishikawa 923-1292, Japan

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ABSTRACT

We demonstrated an acetalization reaction as a versatile method to immobilize aromatic aldehyde molecules on surfaces of metal oxides, silicon dioxide, and indium tin oxide. First, a trimethylsily (TMS) terminated surface was formed using a silylation reaction between a chloride group of trimethylsilychloride and a hydroxyl group of the substrate surfaces. Second, terephthalaldehyde (TPA) was immobilized on the surfaces using an acetalization reaction between the TMS-terminated surface and an aldehyde group of TPA. Results of contact angle, X-ray photoelectron, and ultraviolet absorption spectra revealed that the TPA molecules on the surfaces were well-packed with a high surface density.

1. Introduction

Organic molecules with a thiol group [1], a silanol group [2], a carboxylic acid group [3,4], and a phosphoric acid group [3,4], have been widely used to form a self-assembled monolayer (SAM) on surfaces of gold and metal oxides. The formation of a high-quality SAM is very crucial to modifying electronic states of electrode/organic interfaces [3,4] and to construct next-generation molecular-scale devices [5,6] and biomolecular sensors [7]. In fact, the performance of organic light-emitting diodes [8], organic photovoltaic cells [9], and organic thin-film transistors [5] has been improved through the surface treatment of electrodes with a SAM. On the other hand, we are aiming at using a SAM as a reaction initiator to obtain aligned π-conjugated polymers, where different functional monomer units are alternated by layer-by-layer growth in the direction normal to the substrate surfaces. A π-conjugated polymer of polyazomethine (PAM) is a promising candidate for the layer-by-layer growth because PAM thin films can be obtained from vapor deposition polymerization [10,11] and chemical vapor deposition polymerization [12] of two kinds of monomers, such as terephthalaldehyde (TPA) and *p*-phenylenediamine. For the layer-by-layer growth of the PAM, organic molecules with an aldehyde group or an amine group must be immobilized on the substrate surfaces.

In this study, we demonstrated that an acetalization reaction is a versatile method to form a TPA SAM with an aldehyde group on the surface of indium tin oxide (ITO), which is widely used as an anode for the first time. We found that TPA molecules immobilized on the ITO surfaces using the acetalization reaction are well-packed having a high surface density of 1.71×10^{-5} mol m^{-2}.

The chemical structures of the organic molecules used in this study, trimethylchlorosilane (TMCS) and TPA, are shown in Fig. 1(a) and (b), respectively. The immobilization reaction of the TPA on a substrate using the acetalization is composed of two-step reactions as illustrated in Fig. 1(c): First, trimethylsilyl (TMS)-terminated surface was formed using a silylation reaction between a chloride group (—Cl) of TMCS and a hydroxyl group (—OH) of the substrate surfaces. Second, a TPA-terminated surface was formed using an acetalization reaction between the TMS group and an aldehyde group (–CHO) of TPA. This surface reaction was developed based on the acetalization reaction between an aldehyde compound and a diol compound [13–15].

2. Experimental

Bare quartz substrates and glass substrates coated with a 100 nm ITO layer (substrate size: 25 × 25 × 0.1 mm) were cleaned using ultrasonication in acetone, followed by ultrasonication in detergent, pure water, and isopropanol. After the ultrasonication, the substrates were placed in an UV–O_3 treatment chamber for 30 min to form a hydroxyl group on the surfaces of quartz and ITO (step 1 in Fig. 1(c)). TMCS and TPA were purchased from Tokyo Chemical Industry and Aldrich, respectively and used as received. A 10 mM TMCS solution (dehydrated toluene) and a 10 mM TPA solution (dehydrated dichloromethane) were prepared in teflon containers. The cleaned substrates were soaked in the TMCS solution for 1 h to terminate the substrate surfaces with TMS using a silylation reaction (step 2 in Fig. 1(c)). Then, the TMS-terminated substrates were soaked in the TPA solution for 18 h to immobilize the TPA on the substrate surfaces using an acetalization reaction (step 3 in Fig. 1(c)). After the acetalization, these substrates were cleaned using ultrasonication in pure dichloromethane to remove physisorbed molecules from the substrate surfaces. The silylation and acetalization

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* Corresponding author. Tel.: +81 761 51 1531; fax: +81 761 51 1149.
E-mail address: murata-h@jaist.ac.jp (H. Murata).

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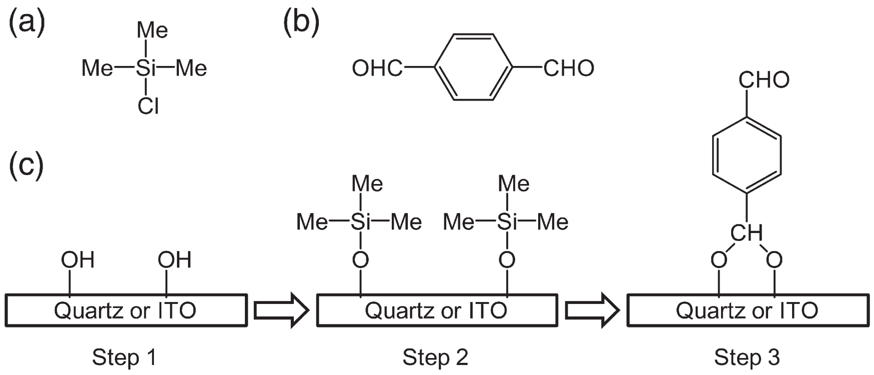

Fig. 1. Chemical structures of (a) TMCS molecule and (b) TPA molecule and (c) schematic illustration of TMS silylation and TPA acetalization on quartz and ITO substrates.

reactions were performed in a nitrogen-filled glove box at room temperature.

The water/substrate contact angles of the TMS-terminated and TPA-terminated substrates were measured using a 10 μl pure water dropped on the substrate surfaces in air. The chemical bonding states of the TMS-terminated and TPA-terminated substrates were examined by using an Al-Kα X-ray of an X-ray photoelectron spectrometer (XPS) (ESCA5600, ULVAC-PHI). A 0.1 μM TPA solution (dehydrated acetonitrile) was prepared and the UV absorption spectra of the TPA-terminated substrates and the TPA solution were measured for comparison using an ultraviolet–visible (UV–VIS) absorption spectrometer (V-570, JASCO). After the measurements, the TPA-terminated substrates were soaked in a solution of a sulfuric acid catalyst (0.1 mM, 20 μl) dissolved in methanol or acetonitrile (10 ml) for 12 h at 55 °C to remove the TPA molecules from the substrate surfaces using a hydrolysis reaction. Then, the UV absorption spectra of the solutions containing the hydrolysed TPA molecules were measured to estimate the surface densities of the TPA molecules immobilized on the ITO and quartz substrates.

3. Results and discussion

The water/substrate contact angles of the surfaces of quartz and ITO terminated with the TMS and the TPA are summarized in Table 1. The contact angles were measured to be ≈0° for the bare quartz and ITO surfaces, 70.3° for the TMS-terminated quartz surface, 73.5° for the TMS-terminated ITO surface, 58.5° for the TPA-terminated quartz surface, and 64.0° for the TPA-terminated ITO surface. The increase in contact angle is attributable to the change of surface energies of the substrates, which is caused by the formation of the TMS and TPA SAMs on the substrate surfaces.

The C 1*s* spectra of the TPA-terminated quartz substrate and the bare quartz substrate were measured using the XPS (Fig. 2). By the peak separation using Gaussian function, it was found that the C 1s spectra were composed of three peaks originating from C–C (255.6 eV), C–O (286.7 eV), and C=O (287.5 eV) (see Table 2). The observation of the C–C and C–O peaks in the bare quartz substrate may be due to unexpected carbon contamination on the quartz surfaces. We found that the C=O peak intensity of the TPA-terminated quartz substrate at 287.5 eV became stronger than that of the bare quartz substrate, indicating that the presence of an aldehyde group on the treated surfaces. These spectral features indicate that the TPA was terminated on the quartz substrate using the acetalization reaction.

We were also able to confirm the reaction of TPA on the TMS-terminated quartz substrate from the UV absorption spectrum of the TPA-terminated quartz substrate (Fig. 3). Although no absorption peak was observed in the spectrum of the bare quartz substrate, the new absorption peak appeared at a wavelength of 255 nm in the spectrum of the TPA-terminated quartz substrate. The similar absorption peak (255 nm) was observed in the spectrum of the TPA solution. The contact angle, XPS, and UV absorption studies clearly indicate that the TPA molecules were immobilized on the quartz substrate using our acetalization reaction. It is well-known that acetal compounds are easily hydrolysed using an acid catalyst. To double check the presence of the TPA molecules immobilized on the quartz substrates, the TPA molecules were removed from the substrate surfaces using a hydrolysis reaction by soaking the substrates in the sulfuric acid solution. We observed that the TPA absorption peak on

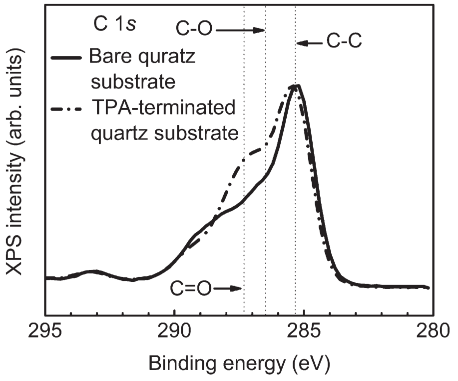

Fig. 2. XPS spectra of C 1*s* peaks of bare quartz substrate and TPA-terminated quartz substrates.

Table 1
Water/substrate contact angles of quartz and ITO substrates terminated with TMS and TPA.

	Bare	TMS-terminated	TPA-terminated
Quartz	≈0°	70.3 ± 0.7°	58.0 ± 0.5°
ITO	≈0°	73.5 ± 0.5°	64.5 ± 1.5°

Table 2
Ratios of C–C, C–O, and C=O peak areas in C 1*s* XPS spectra of TPA-terminated quartz substrate.

	Binding energy (eV)	Area ratio (%)
C–C	285.3	54.9
C–O	286.7	24.8
C=O	287.5	20.3