Molecular Crystals and Liquid Crystals

The Molecular-Ruler Fabrication of Nano-Structures for Nano-Scale Devices: 1. Dielectric Layer-by-Layer Structures

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The Molecular-Ruler Fabrication of Nano-Structures for Nano-Scale Devices: 1. Dielectric Layer-by-Layer Structures

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Nano-scale organic dielectric layers for organic thin film transistor (OTFT) were synthesized by the molecular-ruler method. Molecular-ruler method has been known as a good process to fabricate nano-scale structures for nano-devices with the advantages of low cost and high throughput. In this work, 16-mercaptohexadecanoic acid (16-MHDA) was used to make compact layers on gold substrate by self-assembled monolayer (SAM) and copper (II) was also used as a linker ion between 16-mercaptohexadecanoic acid (16-MHDA) layers. Finally multiple layer-by-layer structures of 16-mercaptohexadecanoic acid (16-MHDA) and copper (II) were fabricated. X-ray fluorescence (XRF) spectroscopy, x-ray photoelectron spectroscopy (XPS), cyclic voltammetry (CV), infrared (IR) spectroscopy and scanning electron microscope (SEM) methods were utilized to verify the character of these structures.

Keywords 16-Mercaptohexadecanoic acid (16-MHDA); layer-by-layer dielectric; molecular-ruler method; OTFT; self-assembled monolayer

1. Introduction

Fabrication of multiple layer-by-layer structures on an appropriate substrate by using self-assembled monolayer (SAM) as a basic layer has been known as an attractive technique in the field of nano-lithography because these structures have great potential in producing the desired nano-structures at molecular level and their functionalities are controllable easily [1,2]. The chemical properties of a substrate could be changed by modifying the surface with appropriate functional groups. Therefore couples of SAM layers have been selected as building blocks of the layer-by-layer structures with linker species [3,4]. Alkanethiol SAM has ability to form well ordered organic molecular layer on gold substrate with good stability because they have bonding character between sulfur and gold and the Van der Waals

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interactions between alkyl chains [5]. For this reason acid-terminated alkanethiols are particularly interesting because they have a special functional group at the end providing a chance of forming different SAM layers on them [6]. 16-MHDA and copper (II) were selected to build up multiple layer-by-layer structures on substrate consisted of 30-nm-thick Au layer on Si wafer. Underneath of this Au layer a 5-nm-thick Cr layer was used as an adhesion promoter. The thiols attached only to the gold made SAM layer first and then the carbonyl end group easily connected to the linker Cu ions [7–9]. This Cu layer is ready to make the second layer of 16-MHDA on itself and so on. Therefore 16-MHDA and copper (II) couples were used in fabricating multiple layer-by-layer structures on the Au substrate. The possibility of fabricating a multiple layer-by-layer structure on bare electrode allows preparing inorganic-organic molecular structures that can passivate the surface of the substrate electrode. Furthermore the thickness of the multiple layer-by-layer structure can be simply controlled by varying the numbers of layers in this structure. Devices adopting OTFT are considered to have distinguished mechanical and electric properties compared to usual devices. Production of flexible integrated circuit depends on flexibility of low cost substrate and manufacturing temperature. Therefore the OTFT devices can be directly applied to flexible display, sensor, electron barcode and RFIC card. In this paper, the formation process of layer-by-layer SAM has been investigated by monitoring a variety of surface analysis techniques.

2. Experimental

16-mercaptohexadecanoic acid (90%, Aldrich), copper (II) perchlorate (98%, Aldrich), absolute ethanol (99.9%, Fisher scientific), acetone (99.9%, Aldrich), hydrochloride acid (35.0 ~ 37.0%, Samchun chemical), nitric acid (61%, Matsuneon), potassium chloride (99%, Aldrich) and potassium ferricyanide (III) (99%, Aldrich) were purchased and used without further purification.

The gold pellet was used to deposit gold layer (~nm thick) on n-type silicon substrate by the vapor deposition method. Cr layer (~5 nm) was used as an adhesion between Au and Si. Finally the substrate has $Au/Cr/SiO_2/Si$ structures. The gold electrodes on silicon wafer were cleaned with three cleaning solutions to obtain uniform and purified surface before SAM fabrication process. Electrodes were washed with diluted aqua-regia (nitric acid and hydrochloride in 1:3 ratio) and rinsed with absolute ethanol and acetone for ~30 minutes respectively. During the cleaning process, DI water (18 MΩ) was also used to rinse out the sample at each stage. Every single cleaning solution was filtered by nylon filter with 0.2 μm pore. The SAM was prepared in the following sequential steps: (1) Gold electrodes were immersed in a 1 mM ethanol solution of 16-MHDA for 30 or 50 min [10]. (2) After each formation time, one electrode was taken out of the SAM solution and rinsed with absolute ethanol and DI water. (3) Each of the SAM electrodes was immersed in a 1 mM ethanol solution of Copper (II) perchlorate from 5 to 10 minutes. (4) Each time the electrode was taken out of the SAM solution, it was rinsed as in step (2). The repetition of steps 1, 2, 3, and 4 would enable us to make multiple layer-by-layer systems with controllable thickness [11,12]. Formation process of these multiple layer-by-layer structures was analyzed with cyclic voltammetry (100B, BAS), infrared spectroscopy (RAMII, Bruker), scanning electron microscope (JSM6700F, JEOL), x-ray photoelectron spectroscopy (AES-XPS, ESCA2000) and x-ray fluorescence spectroscopy (ZSX100e, Rigaku).

3. Results and Discussion

To verify the SAM building process in the nano-scale, the 16-MHDA SAM forma-tion experiments were done following the process described above. The layer-by-layer structures were verified by using various electrochemical and spectroscopic methods. The SAM structure on gold electrodes was confirmed by cyclic voltamme-try which is a well-known method for verifying the formation of well-ordered SAM. After each immersing time, electrode was taken out of the 16-MHDA solution and rinsed thoroughly. The electrode was dipped into the electrolytic solution of $2 \, mM \, K_3Fe(CN)_6$ in deionized water with $0.1 \, M$ KCl as a supporting electrolyte. Cyclic voltammatic tests were done on this electrode. The applied potential was cycled between $-100 \, mV$ and $600 \, mV$ (vs. Ag/AgCl, Sat'd KCl) at a scan rate of $50 \, mV/s$, as shown in Figure 1 [13]. The responding current makes cyclic voltammo-gram. Figure 1(a) shows the cyclic voltammograms depend on the SAM formation time. This was done for finding suitable SAM fabrication time. CV (1) in this figure shows well developed current peak pair due to the redox reaction of $Fe(CN)_6^{3-}$ species at the bare electrode surface. But the electrode covered with 16-MHDA SAM for 30 min shows very small peak pair, CV (2), which is almost irreversible
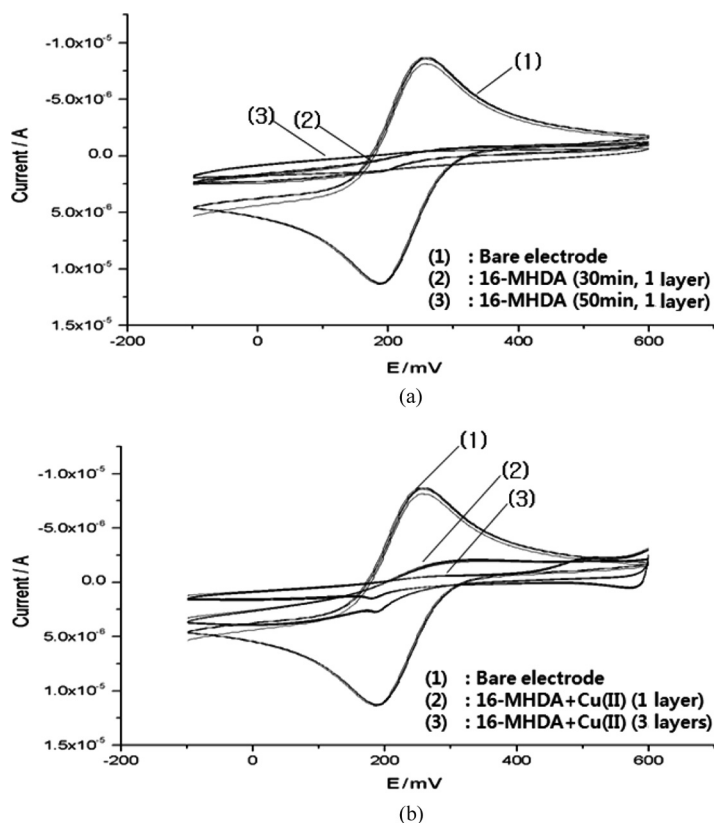

Figure 1. Cyclic voltammograms due to the redox reaction of $Fe(CN)_6^{3-}$ species in $2 \, mM$ $K_3Fe(CN)_6/0.1 \, M$ KCl solution. The shape of CV depends on SAM formation time (a) and number of SAM layers (b).

redox of the same species. After 50 min formation the CV (3) shows no current response except capacitive current. After 16-MHDA SAM formed, the electrode was dipped into copper (II) solution to make a linker layer for 5 min. After rinsing 16-MHDA and copper (II) monolayer fabricated electrode, the electrode was dipped into 16-MHDA solution again to make the second layer of 16-MHDA layer and so on. Electrochemical tests were done for the layer-by-layer structures, as shown in Figure 1(b). As the number of layers increased, the current response is decreased. This means the charge transporting property of these structures decreased as the number of layers increased. The current of the SAM formed electrodes was observed to have more decreasing in current than the bare electrode. Furthermore the more layers were formed, the lower corresponding redox current was detected. This indicated that increase in the number of layers was successfully blocking the gold electrode surface.

Infrared spectroscopic analysis was conducted in order to understand the layer formation process. Figure 2(a) shows IR spectral change that depends on terminal group of multiple layer-by-layer. In this figure, spectrum (2) stands for the sample
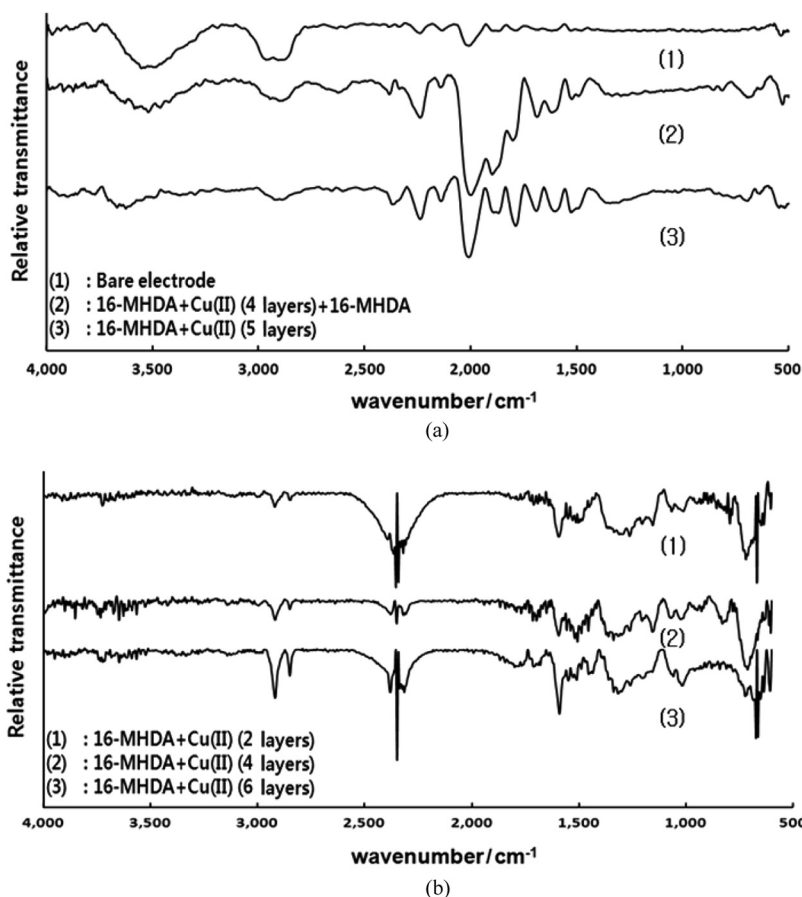

(a)

(b)

Figure 2. IR spectra of SAM with different terminal groups (a) bare electrode (1), carbonyl terminal group (2) and Cu (II) terminal group (3). Number dependent IR spectra (b) two layers (1), four layers (2) and six layers (3).

having carboxyl end group and spectrum (3) is responsible for the sample of copper (II) end group. As we expected spectrum (2) shows the strongest absorption at $1700 \, cm^{-1}$ to $2000 \, cm^{-1}$ region compared to spectrum (1) and spectrum (3) because the carbonyl group was the surface species. For comparison, spectral change due to the change of layer number was shown in Figure 2(b). The spectral change was expected as the number of layers increase. In this, all these electrodes have the same surface species of Cu (II). Therefore absorption spectral difference due to the number of layers with Cu (II) species appeared in this figure. As the number of layers increased, the IR absorption is increased. Figure 2(b) shows increase at $\sim 3000 \, cm^{-1}$ and $1700 \, cm^{-1}$.

The growth of the layer-by-layer structures could be confirmed by using SEM images as in Figure 3. As the multiple layer-by-layer structures formed, the void space between nano-gap electrode is decreased [14]. In this, the change of nano-gap between gold electrodes on Si wafer was used as a measure of the formation of multiple layer-by-layer structures. As a result, decreased gap between the electrodes and increased width of each gold finger electrode were observed. Bare Au finger electrodes of 357 nm width were separated by 29 nm originally. After modifying the electrodes with 5 layer-by-layer structure, the dimensions were changed into 14 nm gap and 372 nm width approximately, as shown in Figure 3(b). This indicates that molecular layer was formed about 15 nm thickness. Based on these SAM images, 16-MHDA and copper (II) were compactly fabricated about 1.5 nm thickness per monolayer [14].

Figure 4 shows the XPS characteristic data for (1) bare gold electrode, (2) 16-MHDA monolayer formed on the gold electrode and (3) 16-MHDA and copper (II) monolayer formed on the gold electrode. XPS intensity due to Au4f of bare gold electrode at 100 eV is much higher than SAM layers formed gold electrode, as shown in spectrum (1) and spectrum (2). On the basis of this result, SAM layer was fabricated on the gold electrode. Cu 2p peak appeared at 933 eV–952 eV in spectrum (3) while no peak was observed at the same position in spectrum (1) and spectrum (2). Comparison of these figures indicates that the SAM layers were successfully formed layer-by-layer structures.
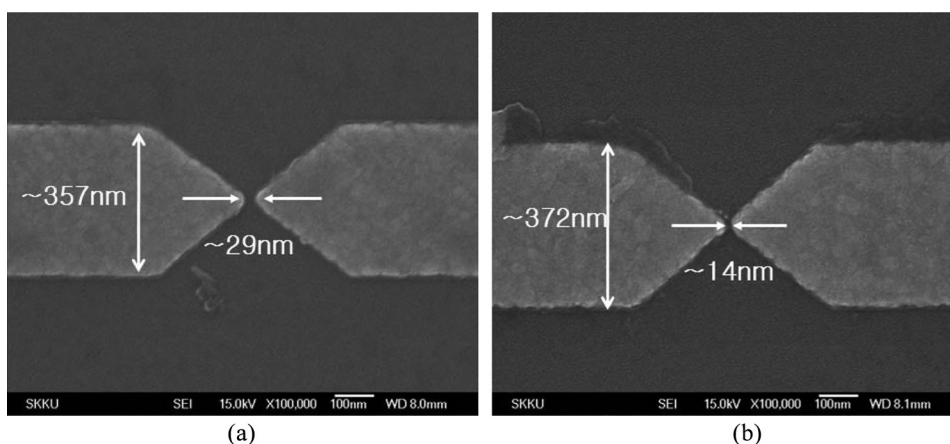

Figure 3. SEM images without (a) and with (b) the layer-by-layer structure.
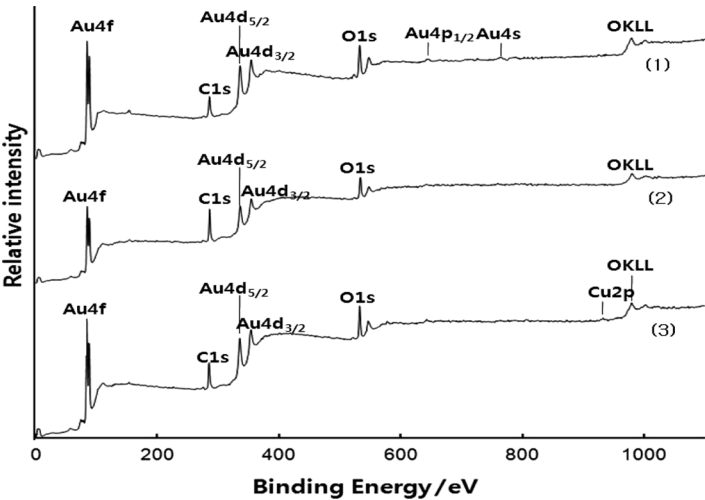
Figure 4. XPS data from different surface species: bare Au electrode (1), 16-MHDA monolayer (2) and 16-MHDA + copper (II) monolayer (3) on the Au electrode.

Figure 5(a) shows XRF data of sulfur atom of two, four, and six layers of SAM on the gold electrodes. As the number of layers increased, the intensity of sulfur was also increased gradually. In the case of copper atom, XRF data show the same result in Figure 5(b). As we expected, K_α intensity of sulfur particularly increased at
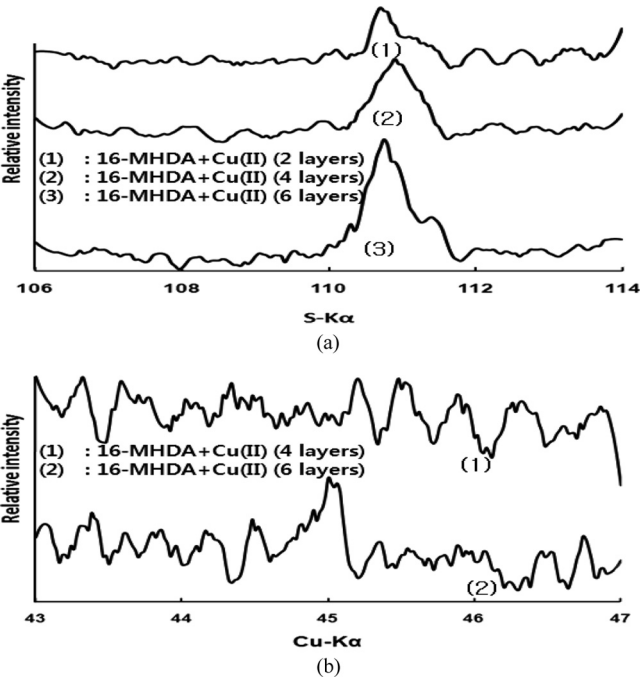

Figure 5. XRF signal depends on the number of layers. Sulfur (a) and copper (b) intensities increase with the number of layers.

110.7–110.9 degree in Figure 5(a) and K_{α} intensity of copper also increased at 45.01 degree in Figure 5(b). These results demonstrate that multiple layer-by-layer structures of 16-MHDA and copper (II) were formed in sequence.

4. Conclusion

We have investigated the fabrication of multiple layer-by-layer structures by formation of SAM layers of 16-MHDA and copper (II) in sequence. This fabrication consists of sequential immersing process of organic species, linker ion, organic species, linker ion, and so forth until the desired thickness is created. The array of carboxylic acid functional group has been shown to cause a surface chelate effect, which tightly binds the copper (II) ions. We could expect that thickness, composition, and orientation of these multiple layer-by-layer structures could be controlled by the varying each layer structure. This molecular-ruler method is considered to be a good way to fabricate sufficiently precise applicable structures in nano-science.

Acknowledgment

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