

Supporting Information for

Nanodielectric Properties of 16-MHDA self-assembled monolayers

Experiment

Materials and equipment

16-mercaptohexadecanoic acid (16-MHDA) ($\geq 99\%$), copper (II) perchlorate hexahydrate ($\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$) (98%), potassium hexacyanoferrate (III) ($\text{K}_3\text{Fe}(\text{CN})_6$) (99%), and potassium chloride (KCl) (99%) were purchased from Sigma-Aldrich. Absolute ethanol (99.9%) was obtained from Fisher Scientific, and sulfuric acid (H_2SO_4) (35.0~37.0%) and hydrogen peroxide (H_2O_2)(34.5%) were received from Samchun. All chemicals were used without further purification. The gold substrates, which were comprised of a 10/150nm-thick layer of Ti/Au on a Si(100) wafer, were prepared using electron beam (e-beam) evaporation. An Ag/AgCl (sat'd KCl) and Pt plate were used as the reference and counter electrode, respectively. The potentials applied to the working electrode during all of the electrochemical experiment were controlled by potentiostat/galvanostat (EG&G M263A). A Fourier-transform infrared (FT-IR, Bruker Tensor 27) spectrometer equipped with an attenuated total reflectance (ATR) apparatus and X-ray photoelectron spectrometer (XPS) was used to confirm the formation of the 16-MHDA SAMs-modified substrate. XPS analysis was conducted using the VG Scientific ESCA 2000 spectrometer with the Al-Mg (twin anode) X-ray source set (15mA and 13kV). The uncontact-mode AFM was conducted with a Park NX10 instrument (Park Systems). I-V and C-f were tested in a variable-temperature probe station (Keithley 4200 Semiconductor Characterization System Unit).

Formation of self-assembled 16-MHDA monolayers

In this study, making 16-MHDA monolayers from a selection of the appropriate materials which could strongly connect two 16-MHDA monolayers was crucial. The simultaneous ease of operation in the connecting process was also needed. As the head and end group of 16-MHDA are thiol and carboxyl, respectively, a copper (II) ion was one of the best choices to connect the two groups. Therefore, the sequential and alternated materials of the organic species 16-MHDA and the coordination of metal ions Cu^{2+} (from copper (II) perchlorate hexahydrate) were used in our experiment.

All solvents were treated by sonication for 5 minutes and blowing in N_2 to remove the oxygen before experimentation. The gold wafer ($1 \times 1\text{cm}^2$) was immersed in a 1 mM 16-MHDA solution of HPLC grade absolute ethanol for 1 hour and then rinsed with absolute ethanol three times. Next, the substrate was immersed in a copper (II) perchlorate solution for 15 minutes to make sure enough copper ion was chelated with the terminal carboxyl group, and then the substrate was washed three times with absolute ethanol. Next, the substrate was again immersed in a 16-MHDA ethanol solution in order for the thiols from 16-MHDA molecules to band onto the Cu^{2+} , thus leaving the carboxyl termini to coordinate with Cu^{2+} in the next process. This process was repeated several times until the desired thickness of SAMs was achieved.

Sandwich junction device fabrication

In this study, a Sandwich junction structure (Metal-molecule-Metal) device was made to test the characteristics of the dielectrics. A gold wafer was used for the bottom metal electrode, and the 16-MHDA layers at different thicknesses were used for the dielectrics layers with a PEDOT/PSS protective layer. The top metal electrode was deposited onto the PEDOT/PSS layer. Before the experiment, the gold wafer (Ti/Au metal on the silicon wafer) was cleaned by immersion in a piranha solution (98% H_2SO_4 / 30% $\text{H}_2\text{O}_2 = 3:1$ v/v) for 3 minutes and then washed by deionized water and ethanol sequentially. Then, it was dried by blowing N_2 at room temperature. Next, the substrate was immersed in a 16-MHDA solution and a copper (II) perchlorate solution

alternately (for the particulars of the SAM formation experimental process, see above). After the SAM was formatted on the gold substrate, a protective PEDOT/PSS layer was spin-coated on top of the SAM at a thickness of about 100 nm. The water-based suspension of PEDOT/PSS was spin coated at 500 rpm for 5 s, then 1000 rpm for 10 s, and finally 4000 rpm for 30 s. The substrates were dried in a vacuum oven at 70°C overnight. The gold top electrodes were directly vapor-deposited (0.1\AA s^{-1}) on the protective layer through a shadow mask ($200\mu\text{m}\times 200\mu\text{m}$) by the e-beam method at a thickness of about 40 nm (Scheme 1).

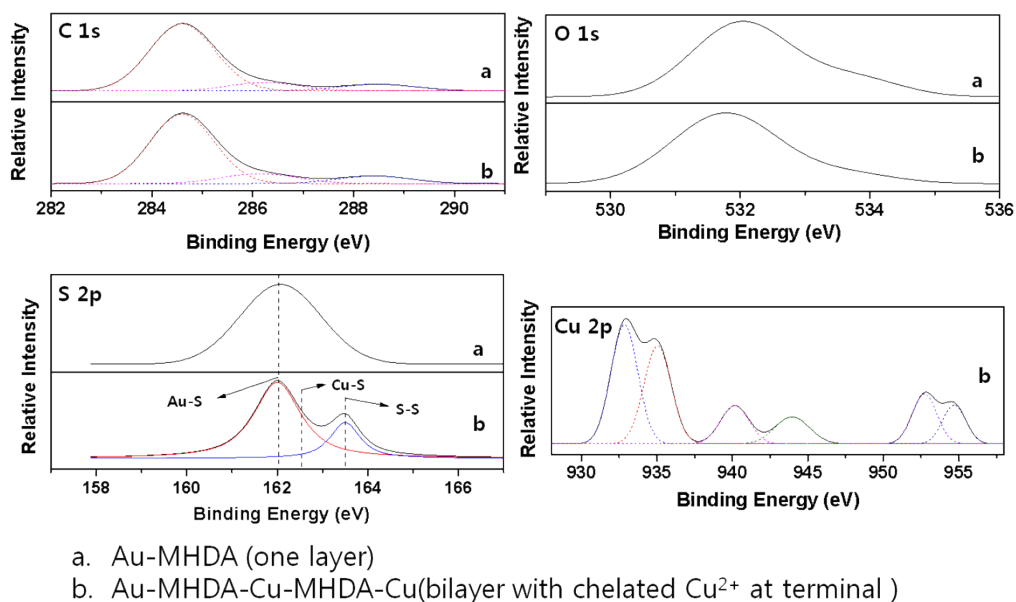


Fig.s1 XPS C 1s, O 1s, S 2p, Cu 2p spectra for growth stages a and b

Fig.s1 showed the C 1s, O 1s, S2p, and Cu 2p regions for samples of 1 layer and 2 layers (terminal with Cu^{2+} which was chelated by $-\text{COOH}$ from the second layer of 16-MHDA) for the 16-MHDA SAMs. Here, all of the spectral analysis (background and peak separation) used mixed Gaussian-Lorentzian functions in a least-squares curve-fitting program.

The C 1s electrons from stage a and b all gave two peaks at 284.6, 286.1, and 288.4 eV. The sharp peak at 284.6 eV corresponded to the main alkyl chain C (R-C-

R). The peak of 286.1 eV was carbon-bonded sulfur, and the broad peak at 288.4 eV consistent with both the -COOH and -COO⁻ groups. The binding energy of O 1s changed from 532.0 eV of the -COOH group to 531.8eV (from stage a to b) appropriated for a symmetrical -COO⁻. When we added Cu(ClO₄)₂ to the SAM film, the adjacent pair of the -COOH terminal groups on the SAM would coordinate with the Cu²⁺. The S 2p peak at 162.0 eV (we have not done the deconvolution to divide the S 2p doublets) could be assigned to the thiolate species (Au-S at 161.9±0.1 eV and Cu-S at 162.4±0.1 eV), and the peak at 163.5eV was the S - S bond, When the second layer formatted, the sulfur in the thiols would be oxidized by Cu²⁺, and then two sulfurs nearby can connect to form disulfides.⁽²⁾ The binding energy at 932.8 and 952.7 eV were attributed to Cu⁺, which was reduced from Cu²⁺ by binding with the -SH or by exposure to the X-ray beam. The peaks appeared at 935.1, 954.7 eV and the satellites peaks at 940.1, 944.0 can make sure that the Cu²⁺ ions existed. These ions were the chelated Cu²⁺ with -COOH at the terminal of SAMs, which were not reduced from +2 to +1 (some Cu²⁺ ions were reduced by the photoelectrons).

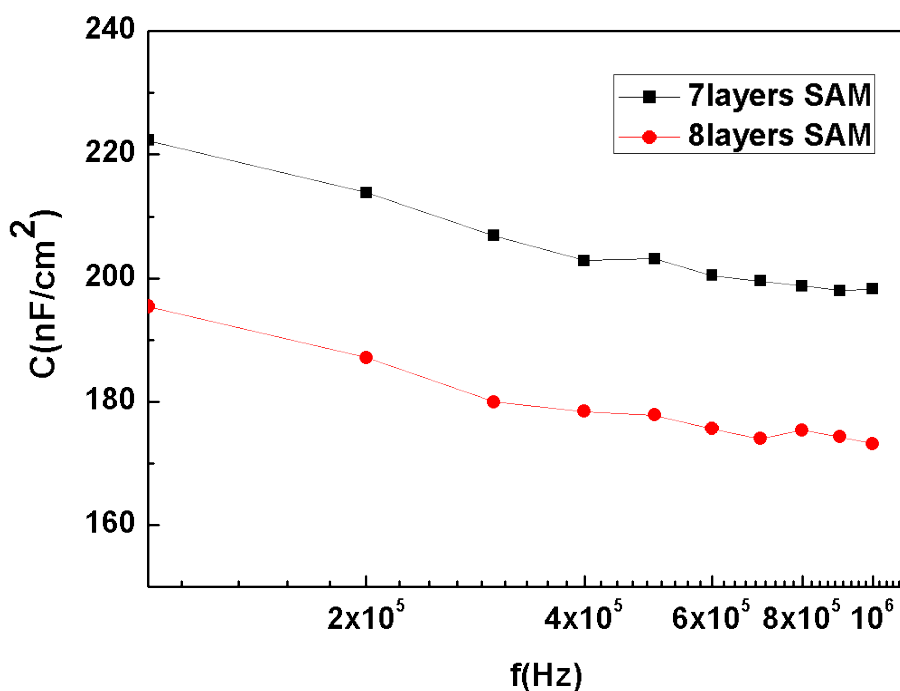


Fig. s2 Frequency (*f*) dependence of the capacitance (*C*) at 1 V between 10⁵Hz and 10⁶Hz for the 7 and 8 layers 16-MHDA

References

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2. M. Brust, P. M. Blass, A. J. Bard, *Langmuir*, 1997, **13**, 5602-5607