

Electrical charging of Au nanoparticles embedded by streptavidin-biotin biomolecular binding in organic memory device

Sung Mok Jung, Hyung-Jun Kim, Bong-Jin Kim, Yong-Sang Kim, Tae-Sik Yoon, and Hyun Ho Lee

Citation: [Applied Physics Letters](#) **97**, 153302 (2010); doi: 10.1063/1.3500824

View online: <http://dx.doi.org/10.1063/1.3500824>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/apl/97/15?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Programmed self-assembly of microscale components using biomolecular recognition through the avidin–biotin interaction](#)

J. Vac. Sci. Technol. B **32**, 06F301 (2014); 10.1116/1.4893075

[Organic memory device with self-assembly monolayered aptamer conjugated nanoparticles](#)

Appl. Phys. Lett. **103**, 083702 (2013); 10.1063/1.4819336

[Organic memory device with polyaniline nanoparticles embedded as charging elements](#)

Appl. Phys. Lett. **100**, 163301 (2012); 10.1063/1.4704571

[Charging phenomena in pentacene-gold nanoparticle memory device](#)

Appl. Phys. Lett. **90**, 042906 (2007); 10.1063/1.2435598

[Negative differential resistance and electrical bistability in nanocrystal organic memory devices](#)

Appl. Phys. Lett. **89**, 252107 (2006); 10.1063/1.2409366



Electrical charging of Au nanoparticles embedded by streptavidin-biotin biomolecular binding in organic memory device

Sung Mok Jung,¹ Hyung-Jun Kim,¹ Bong-Jin Kim,¹ Yong-Sang Kim,² Tae-Sik Yoon,² and Hyun Ho Lee^{1,a)}

¹Department of Chemical Engineering, Myongji University, Gyeonggi 449-728, Republic of Korea

²Department of Nano Science and Engineering, Myongji University, Gyeonggi 449-728, Republic of Korea

(Received 25 May 2010; accepted 20 September 2010; published online 11 October 2010)

In this study, electrical charging phenomena in an organic memory structure using Au nanoparticles (NPs) conjugated with a specific binding mechanism were demonstrated. Monolayer of streptavidin-passivated Au NPs was incorporated on biotin-coated SiO₂ in structure of metal-pentacene-insulator-silicon (MPIS) device. Clockwise and counter-clockwise capacitance-voltage (C-V) hysteresis loops were measured depending on the oxide thickness. For 30 nm, a clockwise C-V hysteresis having memory window of 0.68 V was obtained under (+/−)12 V sweep range, while a counter-clockwise C-V hysteresis having memory window of 6.47 V was obtained under (+/−)7 V sweep range for 10 nm thick oxide. © 2010 American Institute of Physics. [doi:10.1063/1.3500824]

Semiconductor or metal nanoparticles (NPs) are currently a focus of intensive research in the microelectronic field. Due to the small-scale, low cost, and easy fabrication, microelectronic devices based on the NPs has been widely developed.^{1–3} Particularly, the NPs-incorporated organic memory devices have been investigated in comparison with complementary metal-oxide-semiconductor (CMOS) device.^{1–6} Their fabrication methods include polymeric blend of Au NPs,^{1,2} polymeric nanorods or nanopillars having Au NPs at the edge,³ and Langmuir–Blodgett films with intervening Au NPs between pentacene and dielectric.^{4,5} However, the polymeric blending method has a limitation in controllability of distribution and location of the Au NPs.^{1,2} The nanorod or nanopillar formation in Ref. 3 need complicated processes along with the repetitive Au NPs adsorption steps.³ Recently, the self-assembled monolayers of the Au NPs have been reported to show a great potential for memory applications due to its simplicity.^{4–7} The Au NPs as charging elements showed successful hysteresis behaviors in the capacitor structure^{4–6} or were performed as charging layer in “floating gate.”⁷

Biomolecular systems have been employed to fabricate organic memory devices in the previous reports.^{8–10} The NPs including protein⁸ and viruses including NPs (Refs. 9 and 10) have been demonstrated to fabricate the organic memory devices. However, the protein molecules hybridized in NPs were nonspecifically bound to the hydrophilized SiO₂ surface.⁸ In addition, the hybridized protein molecules were finally eliminated.⁸ In the virus systems, the size distribution of Pt NPs synthesized in the virus wires could not be precisely controlled. Moreover, the virus wires were randomly mixed in polymer blend to fabricate memory device.^{9,10} Therefore, if strong, specific, and selective interaction such as streptavidin-biotin binding is to be used to form a monolayer of NPs, it will be advantageous.

In this study, we accomplished a memory device using a strong and selective binding mechanism between the streptavidin-capped Au NPs and the biotin coated on SiO₂

surface. By changing parameter of binding process, for example, the dip coating time, the degree of monolayer formation with Au NPs could be controlled. Coating of biotin (biotinylation) on SiO₂ surface and evaluation of the attachment of streptavidin were reported to be investigated using Fourier transformed infrared (FTIR).¹¹ In addition, the process for capping the Au NPs with streptavidin was reported to be easily performed.¹²

The Au NPs was purchased from British bio cell international (5×10^{13} particles/mL) with diameter of 5 nm in H₂O without any passivation. The Au NPs solution was diluted with 200 μ g/mL streptavidin (Sigma) solution having a 1:3(vol) ratio. The mixture was incubated at room temperature for 12 h, then, centrifuged to collect streptavidin-coated Au NPs selectively with filter microcentrifuge tube (vivaspin 500, Cole Palmer). Then, the filtered Au NPs were resuspended in deionized (DI) water. To fabricate metal-pentacene-insulator (SiO₂)-silicon (MPIS) structure, 10 and 30 nm thick thermal grown SiO₂ were formed on p-type silicon (10–15) Ω cm. Then, the SiO₂ surface was functionalized with 3-aminopropyl-triethoxysilane (APTES) by immersing in 5 vol % of APTES in ethanol for 3 h. The prepared amine coated SiO₂ substrate was dipped into the N-hydroxysuccinimido (NHS)-biotin solution (100 μ g/mL, Sigma) for 1 h to form bonds between the APTES and the biotin. Then, the streptavidin-coated Au NPs were assembled

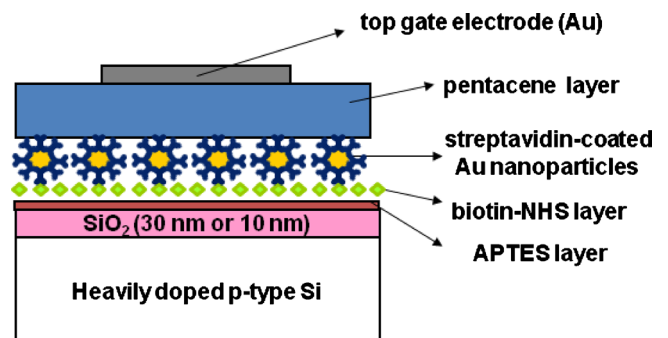


FIG. 1. (Color online) Schematic of nonvolatile MPIS memory device.

^{a)}Electronic mail: hyunho@mju.ac.kr.

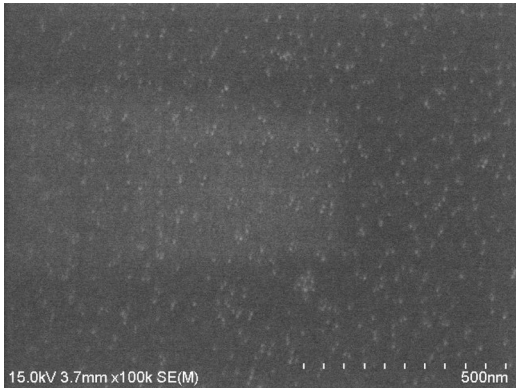


FIG. 2. FESEM image of monolayered streptavidin coated Au NPs on the surface of biotinylated surface.

on the biotinylated surface by immersing the substrates for 12 hrs, and subsequently rinsing with DI water. After the Au NPs assembling, a 60 nm thick pentacene and top Au electrode (0.5 mm diameter) were deposited via sequential evaporation. Chemical bonds were confirmed by attenuated total reflection FTIR. The monolayered Au NPs was analyzed by field-emission scanning electron microscopy (FESEM, JEOL JSM 7000F) and confirmed by measurement of zeta potentials with an electrophoretic light scattering spectrophotometer (ELS 8000, Otsuka). Capacitance-voltage measurements were performed by Agilent 4284A at the frequency of 1 MHz.

Figure 1 shows a schematic diagram of the nonvolatile MPIS memory device. Figure 2 shows FESEM image of the monolayered streptavidin-coated Au NPs on the biotinylated oxide surface. Based on the SEM image, a spatial density of individual Au NPs could be counted in average as $5.47 \times 10^{10}/\text{cm}^2$ with standard deviation of $1.2 \times 10^9/\text{cm}^2$. Since the charging effect is expected from the individual Au NPs, the approximate counting of the particles' bindings can be correlated with the resultant performance of device.

Figure 3 shows the FTIR spectra of a surface deposited by the streptavidin-coated Au NPs and a surface where the streptavidin-coated Au NPs were desorbed by a harsh ultrasonication rinsing. Characteristic peaks at 1130 and

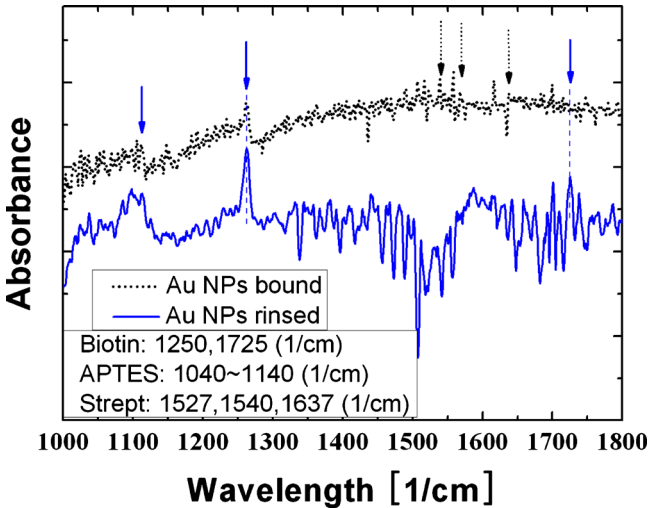


FIG. 3. (Color online) FTIR spectra of surface deposited by streptavidin-coated Au NPs and surface where the streptavidin-coated Au NPs were removed by harsh DI water rinsing of ultrasonication.

TABLE I. Surface zeta potentials of SiO₂ surface and biotinylated surface with streptavidin Au NPs.

Surface (measured with streptavidin-coated Au NPs having zeta potential of -12.73 mV at pH 7.0)	SiO ₂ surface	Biotinylated surface
Surface zeta potential (mV)	-31.39	-17.09

1725 cm⁻¹ for biotin are not detected in Fig. 3 on the Au NPs deposited surface, since the biotin molecules are screened by the NPs. In addition, the peaks (near 1040 and 1140 cm⁻¹) representing for Si-O-Si of APTES layer are also screened by the Au NPs. Instead, peaks representing for amide bonds (1527, 1540, and 1637 cm⁻¹) of streptavidin molecule are detected on the Au NPs deposited surface.^{11,12} Through a harsh rinsing of the Au NPs layer, the biotin bands at 1130 and 1725 cm⁻¹ are restored due to the Au NPs desorption. In addition to the FTIR analysis, surface zeta potentials of SiO₂ surface and the biotinylated surface with the streptavidin-coated Au NPs were measured in Table I. It shows that the surface zeta potentials on the SiO₂ surface and the biotinylated surface were measured as -31.39 mV and -17.09 mV, respectively, measured with the streptavidin-coated Au NPs having -12.73 mV zeta potential. The decrease of absolute value (31.39-17.09 mV) of the surface zeta potentials indicates a strong binding effect of the streptavidin to the biotinylated surface.

Figure 4 shows clockwise hysteresis loops of capacitance-voltage (C-V) from the device fabricated by the streptavidin-coated Au NPs monolayer. The memory devices have 30 nm thick SiO₂. Clockwise hysteresis was found from positive charge (hole) trapping in Au NPs which was injected from the top electrode.⁶ A C-V hysteresis window of 0.33 V was obtained with forward and backward sweep from -10 to +5 V. By increasing sweep range up to (+/-)12 V, the hysteresis window became 0.68 V as shown in Fig. 4. When the top electrode is positively biased, the positive charge density should increase at the pentacene/SiO₂ interface by the hole transport from top electrode resulting in shift of C-V curve to the negative bias. Therefore, a clockwise hysteresis is ob-

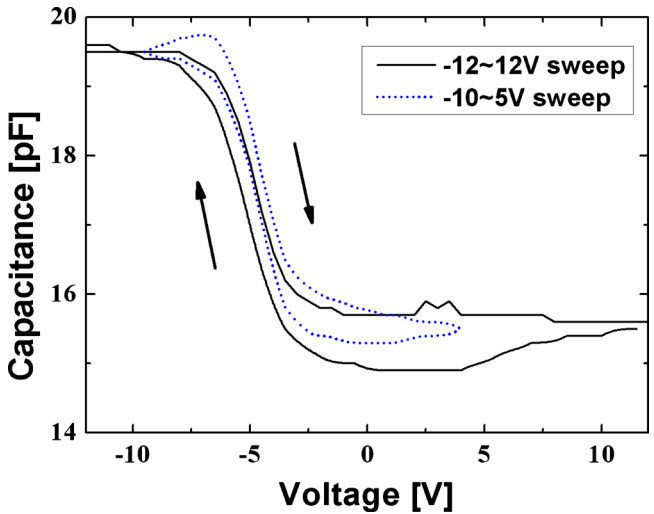


FIG. 4. (Color online) Clockwise C-V characteristics of the memory device having 30 nm thick SiO₂ with Au NPs layer.

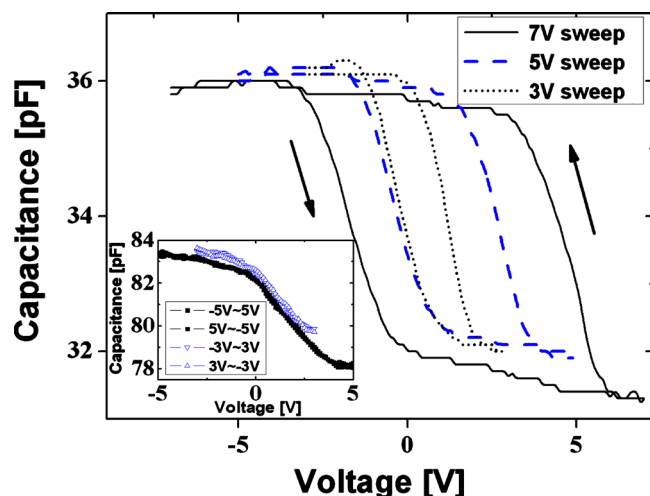


FIG. 5. (Color online) Counter-clockwise C-V characteristics of the memory structure having 10 nm SiO₂ with Au NPs layer under (+/-)3, (+/-)5, and (+/-)7 V sweep ranges.

served, which indicates a hole trapping at the Au NPs since the 30 nm SiO₂ layer is too thick for the charge transport from the Si.^{6,13} The charge transport is typically determined by several factors including effective electric field, Schottky barrier height, conduction and valence band offset, and hopping trap density, etc.^{1,13,14} It is known that the barrier height for hole injection (0.47 eV) and for electron injection (1.17 eV) at top electrode/pentacene interface is lower than 3.5 eV for the electron injection at the SiO₂/Si interface.^{13,14} As a result, the hole transport from top electrode to the Au NPs through pentacene is more efficient.

To confirm the specific binding of the streptavidin Au NPs on the biotinylated surface, a separate MPIS device having nonspecific binding with bovine serum albumin (BSA)-coated Au NPs was prepared. The C-V was demonstrated in the inset to Fig. 5 showing that no hysteresis was detected. When the SiO₂ thickness is reduced to 10 nm in Fig. 5, the C-V characteristics show the hysteresis in the counter-clockwise direction. After the forward and backward sweep from -3 to +3 V, the flatband voltage (V_{FB}) was positively shifted due to the charge or hole trapping resulting in ΔV_{FB} of 1.33 V. For (+/-)5 V sweep, the V_{FB} after the forward sweep was not significantly different from the V_{FB} at the range of (+/-)3 V sweep. However, the sweep voltage in the range of (+/-)5 V induces the hysteresis resulting into ΔV_{FB} of 3.07 V.

The ΔV_{FB} can be approximately given by an Eq. (1)

$$\Delta V_{th} = \frac{Q_{NPs}}{C_{MPIS}}, \quad (1)$$

where Q_{NPs} is the total charges trapped in the NPs and C_{MPIS} is the capacitance of the reference MPIS device without the NPs.¹⁶ With the ΔV_{FB} of 1.33 V of (+/-)3 V sweep, the total charges trapped in NPs is calculated with C_{MPIS} (=22 pF) is 2.93×10^{-11} C. It corresponds to a spatial charge density of $7.31 \times 10^{10}/\text{cm}^2$ if it is assumed that one charge occupies one Au NP. Since the spatial charge density counted from the FESEM was $5.47 \times 10^{10}/\text{cm}^2$ in Fig. 2, the

charge storage effect by one Au NP should be higher than one charge.¹⁴⁻¹⁶

The counter-clockwise nature comes from a mechanism that holes were injected from the accumulation region of the p-type Si or electrons were injected through the thin oxide. As sweep range was increased to (+/-)7 V, the V_{FB} was shifted negatively or positively depending on the forward or backward sweep direction unlike the cases of (+/-)3 and (+/-)5 V sweep. The ΔV_{FB} was measured as 6.47 V. These results indicate that the charge transport from p-type Si is more efficient. The thicknesses of the tunnel oxide have been reported to range from 4 nm to 8 nm for Au nanocrystal embedded cMOS device, which reasonably explains that charges could transport through the SiO₂.¹⁶ However, it is not clear why the electron charging is dominant with the 10 nm SiO₂ since the oxide is thick enough that tunneling can work.^{5,14-16} One possible reason is that the 10 nm SiO₂ was grown at relatively low temperature of 850 °C resulting in somewhat leaky oxide.⁵

In summary, the fabrication of organic memory device using streptavidin-functionalized Au NPs has been demonstrated. The C-V characteristics of the devices were shown to exhibit hysteresis loops, which indicate net charge trapping effects in the Au NPs. It shows both clockwise and counter-clockwise C-V hysteresis depending on the thickness of dielectric oxide.

This work is financially supported by the Ministry of Knowledge Economy (MKE) of Korean Government and Korea Institute for Advancement in Technology (KIAT) through the Workforce Development Program in Strategic Technology (2008-H08-025).

¹A. Prakash, J. Ouyang, J.-L. Lin, and Y. Yang, *J. Appl. Phys.* **100**, 054309 (2006).

²J. Ouyang, C.-W. Chu, D. Sieves, and Y. Yang, *Appl. Phys. Lett.* **86**, 123507 (2005).

³H. P. Wang, S. Pigeon, R. Izquierdo, and R. Martel, *Appl. Phys. Lett.* **89**, 183502 (2006).

⁴S. Paul, C. Pearson, A. Molloy, M. A. Cousins, M. Green, S. Kolliopoulou, P. Dimitrakakis, P. Normand, D. Tsoukalas, and M. C. Petty, *Nano Lett.* **3**, 533 (2003).

⁵M. F. Mabrook, C. Pearson, D. Kolb, D. A. Zeze, and M. C. Petty, *Org. Electron.* **9**, 816 (2008).

⁶W. L. Leong, P. S. Lee, S. G. Mhaisalkar, T. P. Chen, and A. Dodabalapur, *Appl. Phys. Lett.* **90**, 042906 (2007).

⁷C. Novembre, D. Guerin, K. Lmimouni, C. Gamrat, and D. Vuillaume, *Appl. Phys. Lett.* **92**, 103314 (2008).

⁸A. Miura, R. Tsukamoto, S. Yoshi, I. Yamashita, Y. Uraoka, and T. Fuyuki, *Nanotechnology* **19**, 255201 (2008).

⁹R. J. Tseng, C. Tsai, L. Ma, J. Ouyang, C. S. Ozkan, and Y. Yang, *Nat. Nanotechnol.* **1**, 72 (2006).

¹⁰N. G. Portney, A. A. Martinez-Morales, and M. Ozkan, *ACS Nano* **2**, 191 (2008).

¹¹N. A. Lapin and Y. J. Chabal, *J. Phys. Chem. B* **113**, 8776 (2009).

¹²H. K. Park, Y. T. Lim, J. K. Kim, H. G. Park, and B. H. Chung, *Ultramicroscopy* **108**, 1115 (2008).

¹³F. Amy, C. Chan, and A. Kahn, *Org. Electron.* **6**, 85 (2005).

¹⁴J. Robertson, *J. Vac. Sci. Technol. B* **18**, 1785 (2000).

¹⁵T.-S. Yoon, J.-Y. Kwon, D.-H. Lee, K.-B. Kim, S.-H. Min, D.-H. Chae, D. H. Kim, J. D. Lee, B.-G. Park, and H. J. Lee, *J. Appl. Phys.* **87**, 2449 (2000).

¹⁶P. H. Yeh, L. J. Chen, P. T. Liu, D. Y. Wang, and T. C. Chang, *Electrochim. Acta* **52**, 2920 (2007).