矽晶片上之硒化鎘與金奈米粒子感光元件設計與製程

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摘要

在這篇論文中，我們運用 5 nm 粒徑之硒化鎘奈米粒子及 15 nm 粒徑之金奈米粒子，透過庫倫吸引力，建構奈米感光元件於矽晶片上。為了產生庫倫吸引力於矽晶片奈米粒子之間，我們在矽晶片上之二氧化矽表面產成一層化學物質，N-[3-(trimethoxysilyl)propyl]-ethylene diamine (TMSPED)。這樣的化學分子一端與二氧化矽產生穩定的分子鍵 (covalent bond)，另外一端有氨基 (amino groups)，經過質子化 (protonation) 後可帶正電。將黏有 TMSPED 的矽晶片浸泡在含有金奈米粒子的水溶液中，TMSPED 的正電會吸引金奈米粒子表面的正電，進而將金奈米粒子黏在晶片上。接下來我們將黏有金奈米粒子的矽晶片浸泡在表面含有帶正電之硒化鎘奈米粒子溶液。同樣地，透過庫倫吸引力將硒化鎘奈米粒子黏金奈米粒子表面上。為

了要使硒化鎘奈米粒子帶正電，我們在它表面上在生成 4-(2-Aminoethyl)phenol (Tyramine) 分子。理論上，經過一次次重複的組裝過程，我們能形成含有多層硒化鎘奈米粒子及金奈米粒子的奈米結構在矽晶片上。接著我們在矽晶片上之電極兩端加上電壓，並在有照 375 nm 光線或是完全黑的情況下，量測流過奈米感光元件的電流。實踐結果發現，在照光後，在各種電壓下有固定約 2 nA 的電流增加。這樣的特性主要來自於硒化鎘奈米粒子與金奈米粒子間之 “nano-Schottky-diode” 結構。除此之外，在同樣的寬度，越長的電極能量到越大的電流變化。

The Design and Fabrication of Photo-Sensing Nanodevice Composed of CdSe and Au Nanoparticles on Silicon Chip

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ABSTRACT

In this work, we used approximately 5 nm diameter CdSe nanoparticles (NPs) and 15 nm diameter Au NPs to fabricate the photo-sensing nanodevice on silicon oxide substrate by ionic interaction, where Au NPs serve as bridges to connect between CdSe NPs. To introduce Coulombic attraction between NPs and substrate, the silicon oxide surface is modified by N-[3-(trimethoxysilyl)propyl]-ethylene diamine (TMSPED), which provides positive charged amino ($-NH_3^+$) groups to attract negative ($-COO^-$) charged Au NPs. Then, the Tyramine (4-(2-Aminoethyl)phenol)-modified CdSe NPs that have positive charged amino groups on

the particle surface are assembled onto Au NPs. Theoretically, the assembly process can be repeated for several times to form multi-layers structure of Au and CdSe NPs. The overall fabrication process is observed by SEM. Finally, the nanodevice is fabricated on silicon oxide surface between Al electrodes of TSMC 0.35 贡m chip. By applying voltage bias across the electrodes, we measured the photocurrent flowing through the nanodevice after illumination of 375 nm laser diode. The experimental results showed that after illumination, there was constantly about 2 nA increment to the current measured in dark for each voltage bias. This I-V behavior mainly results from the “nano-Schottky-diode” structure between CdSe and Au NPs. Besides, with the same width, the electrodes with longer length will have larger variation of photocurrent after illumination.

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誌於　風城交大　2004 秋

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CHAPTER 2

Table 2.1 The voltage biases of CMOS sensing circuit for simulation results shown below.

CHAPTER 4

Table 4.1 The voltage biases of CMOS sensing circuit for this measurement results shown below.

FIGURE CAPTIONS

CHAPTER 1

Fig. 1.1 Chemistry is the central science for further applications such as material science and biotechnology. The combination of advanced materials and tailored biomolecules will produce the future nanodevices [1].

Fig. 1.2 The top-down processes will have their limit below 100 nm, and the bottom-up processes will also have a limit at 2~5 nm. The gap will be filled by nanoclusters and biomolecules [1].

Fig. 1.3 The overall idea of Ag-Au NPs networks formation by taking advantage of the interaction between antibodies and low molecular weight hapten groups. Bivalent linkers with terminal hapten groups, either mono-specific 8 or bi-specific 9, allow the directed assembly of homo-oligomeric (a) or hetero-oligomeric (b) structure, respectively. The TEM images (c) were obtained from colloidal Au/antibody aggregates before and after the addition of linker 8 [1].

Fig. 1.4 (a) ~15 nm diameter Au NPs modified with alkanethiol-12 base oligomers are hybridized to the oligonucleotide linkers of varying duplex spacer length (24, 48, 72 base pairs). (b) The TEM images of DNA-linked Au NPs aggregates 1-3 are shown. (A) A portion of a 24 base linked aggregate **1**. (B) A higher magnification image of the area in part A. (C) A 48 base linked aggregate **2**. (D) A higher magnification image of the area in part C. (E) A 72 base linked aggregate **3**. (F) A higher magnification image of the area in part E. Scale bars for each image are shown at the bottom of the micrograph [2].

Fig. 1.5 Specific binding of EcoRI conjugated NPs to single λ-DNA molecules. Image (A) is a stretched DNA without binding particles. Images (B) to (F) show single NPs bound to sites 1-5. *N* denotes the normalized experimental position for bound particles [3].

CHAPTER 2

Fig. 2.1 Density of states in metal (A) and semiconductor nanocrystals. In each case, the density of states is discrete at the band edges. In metal, the Fermi level is in the center of a band. As a result, *kT* will exceed the level spacing even at low

temperature and small size. In semiconductor, the Fermi level lies between two bands, so that there is large level spacing even at large size. The HOMO-LUMO gap increases as the semiconductor nanocrystals become smaller (bellow 10 nm) [4].

Fig. 2.2 (a) Illustration of a STM tip-single metal NP-insulator coated gold substrate double tunnel junction and corresponding equivalent circuit. (b) Current versus voltage for a single galvinol-coated Au NP acquired in aqueous solution at pH 5. Insect shows an STM image of the sample. Tip was coated with Apiezon wax and gold substrate was coated with hexanethiol [7].

Fig. 2.3 The cross sectional figure of photo-sensing nanodevice on CMOS sensing chip

Fig. 2.4 The schematic of CMOS sensing circuit.

Fig. 2.5 The Hspice simulation of CMOS sensing circuit.

Fig. 2.6 The simulation result of output versus Rt, the resistance value of photo-sensing nanodevice, is shown above. When the resistance of Rt is below 4.85 MΩ, the output will saturate because Mcm12 will leave the saturation region, entering triode region.

CHAPTER 3

Fig. 3.1 The overall construction process of photo-sensing nanodevice by DNA hybridization system on silicon chip substrate is shown above. (a) The cross-section figure of the surface of silicon chip designed for photo-sensing nanodevice construction, (b) The surface of silicon oxide region after TMSPED (or APTES) modification, (c) The assembly process of CdSe NPs on silicon oxide substrate, (d) The connection between DNA primer and CdSe NPs, (e) The assembly of Au NPs on CdSe NPs by self-assembly process and (f) The nanodevice structure after repeated assembly process.

Fig. 3.2 The TEM analysis of Au NPs with diameter range from 20 nm~40 nm is shown above. (The photo is obtained from *Global Nano Tech. Inc., Taipei*)

Fig. 3.3 The typical UV-visible spectrum of Au NPs suspension in water is shown above. There is a minor peak at 530 nm, which is usually used to determine the concentration of NPs. The concentration here is about 123 ppm (623 μM).

Fig. 3.4 The original DTNB solution at pH 8 is transparent and achromatic. Then, the primers with thiol groups are added into the solution. After the disulfide bond (-S-S-) is attacked by the thiol group of primer, the color of solution will become yellow and the UV-visible spectrum will have an increment at 400 nm due to TNBs

presented in the solution.

Fig. 3.5 The UV-visible spectrums of the three samples are shown above. There is an obvious increment at 260 nm and 400 nm in the spectra due the addition of primers.

Fig. 3.6 After standing for 10 minutes, the color of three samples, "DTNB + primer1", "DTNB + primer2", and "DTNB only" (form right to left) are shown above.

Fig. 3.7 The original Au NPs water suspension was "washed" by the method illustrated above.

Fig. 3.8 The process of conjugating the Au NPs with two complementary primers is shown above. Sam3, Sam1DNA, and Sam2DNA are compared with the experimental results, Sam1s and Sam2s.

Fig. 3.9 The UV-visible absorbance spectrums of Sam1,2,3, Sam1s,2s, Sam1DNA, and Sam2DNA are shown above. We can obviously identify the decrement at OD-260 after centrifugation because the DNA primers attached to the Au NPs are brought to the bottom of tube, resulting in the lower concentration of primers in the supernatant. While measuring the UV-visible absorbance spectrum, all the concentration of the samples were diluted to 30/430 of its original value by adding 400 μL of the phosphate buffer to 30 μL of the sample solution.

Fig. 3.10 The figure above shows the "washing process" to remove excess DNA primers of both samples before mixing them.

Fig. 3.11 The right and middle ones are the samples where Au NPs suspensions are labeled with DNA primer1 and 2 respectively, while the left one is the mixture of the right and middle. As we can see, there is obvious precipitation in the mixture due to self-assembly process between promer1 and 2, and the color of suspension changes from purplish red to light blue.

Fig. 3.12 The structure of TOPO-coated CdSe NP and MUA-modified CdSe NP. The covalent Se-S bond between MUA and CdSe NP is more stable than the ionic or Van der Waals bond between TOPO and Cd site on CdSe NPs.

Fig. 3.13 The overall and detailed process of conversion of oil-soluble TOPO-coated CdSe NPs to water-soluble MUA-modified CdSe NPs is shown above.

Fig. 3.14 The conceptual diagram of the conjugation of DNA primers with MUA-modified CdSe NPs is shown above.

Fig. 3.15 The detailed assembly process of Au NPs on gold substrate is shown above. The purified Au NPs suspension was prepared by the method illustrated in Fig. 3.7.

Fig. 3.16 The SEM images of the Au NPs modified gold substrate by DNA self-assembly process with 50k, 100k and 150k magnification. Note that the diameter of the Au NPs (synthesis form physical method) is in the range of 20~40 nm. To increase the resolution of images, 3 nm thick Pt layer is placed on the surface to increase conductivity of samples.

Fig. 3.17 The conceptual diagram of TMSPED and APTES modifying the silicon oxide surface is shown above. (a) Before modification, the H_2O molecules will attack the Si of TMSPED or APTES, competing with the –OH group on silicon oxide. (b) After modification, the TMSPED or APTES will form stable covalent bond with the silicon oxide.

Fig. 3.18 The SEM images of CdSe NPs modified silicon oxide substrate with 50k, 100k, 150 magnification. Note that the diameter of most CdSe NPs is less than 10 nm. To increase the resolution of images, 3 nm thick Pt layer is placed on the surface to increase conductivity of samples.

Fig. 3.19 The overall construction process of photo-sensing nanodevice by Coulombic force system on silicon chip substrate is shown above. (a) The cross-section figure of the surface of silicon chip designed for photo-sensing nanodevice construction, (b) The modification of TMSPED (or APTES) on silicon oxide surface and the protonation of amino ($-NH_3^+$) groups, (c) The assembly of approximately 15 nm diameter Au NPs on silicon oxide substrate by ionic interaction, (d) The assembly of approximately 5 nm diameter Tyramine-modified CdSe NPs on silicon oxide substrate by ionic interaction, and (e) The formation of photo-sensing nanodevice structure after repeated assembly process.

Fig. 3.20 The detailed Tyramine modification process of HDA-coated CdSe NPs is shown above.

Fig. 3.21 (a) The close photographs of 100 μL of approximately 15 nm diameter Au NPs solution + 100 μL DI water (left) and 100 μL of approximately 5 nm diameter CdSe NPs solution + 100 μL DI water (right). The Au NPs solution was in deep red while the Tyramine-modified CdSe NPs solution was in yellow. (b) The close photographs of the mixture of 100 μL Au NPs solution and 100 μL Tyramine-modified CdSe NPs solution just after mixing (right), the mixture after standing 6 hrs (middle) in room temperature, and the mixture after standing 5 days in room temperature (left). As we can see, the color of mixture just after mixing was like that of Au NPs solution. However, after 6 hrs, it became dark purplish red. After 5 days, there was obvious precipitate at the bottom and the supernatant became pale yellow.

Fig. 3.22 (a) The TEM images of approximately 15 nm diameter Au NPs (left) and approximately 5 nm diameter Tyramine-modified CdSe NPs. (b) The TEM images of the mixture of Au and Tyramine-modified CdSe NPs after standing 24 hrs (Fig. 3.20 (b)-middle) The right is larger magnification of part of the left. (c) The UV-visible spectrum of An NPs solution. (d) The UV-visible spectrum of original HDA-coated CdSe NPs solution in organic solvent.

Fig. 3.23 The close photographs of SiO2/Si wafer fragments of different level assembly

process. (right 1) blank SiO2/Si wafer fragment. (right 2) Au NPs on SiO2/Si wafer fragment. (right 3) CdSe NPs + Au NPs on SiO2/Si wafer fragment. (right 4) Au NPs + CdSe NPs + Au NPs on SiO2/Si wafer fragment. (right 5) Cdse NPs + Au NPs + CdSe NPs + Au NPs on SiO2/Si wafer fragment. (right 6) Au NPs + CdSe NPs + Au NPs + CdSe NPs + Au NPs on SiO2/Si wafer fragment.

Fig. 3.24 The SEM images (50k magnification) of photo-sensing nanodevice structure of different level construction are shown above. Each SEM image has its corresponding close photographs in Fig. 3.22.

Fig. 3.25 The SEM images (150k magnification) of photo-sensing nanodevice structure of different level construction are shown above. Each SEM image has its corresponding close photographs in Fig. 3.22.

CHAPTER 4

Fig. 4.1 The layout of the CMOS sensing chip is shown above. The chip is 1.35 mm * 1.35 mm and has 48 pins. There are six identical CMOS sensing circuits, (1)~(6).

Fig. 4.2 The cross section figure of electrodes structure is shown above, where the four layers of metal lines are connected by vias. The passivation window in this work is 86 μm * 86 μm. The silicon oxide region between Al electrodes has different shapes. The length of the region is ranging from 0.8 μm to 15 μm.

Fig. 4.3 (a) The SEM image of the 13 electrodes. (b) The size (width * length between electrodes) table of the corresponding 13 electrodes. The central 6 electrodes, (1)~(6), are connected to the six identical CMOS sensing circuits. The rest seven electrodes are connected directly to pads for direct measurement.

Fig. 4.4 The measurement results of CMOS sensing circuit are shown above, where It means the current following through the Rt. In this measurement, instead of changing Rt, we change the Vbias to simulate the changing Rt for convenience in measuring. The value of Vip is very close to Vin = 1.355 V, which means the gain of negative feedback loop is large enough to lock Vip with Vin.

Fig. 4.5 The measurement result of output versus Vbias.

Fig. 4.6 The SEM images (with different magnification) of blank electrodes (a) short and (b) wide.

Fig. 4.7 The SEM images (with different magnification) of Au NPs modified electrodes (a) short and (b) wide.

Fig. 4.8 The SEM images (with different magnification) of Au NPs + CdSe NPs + Au NPs modified electrodes (a) short and (b) wide.

Fig. 4.9 The overall experimental procedure of fabrication and measurement of

photo-sensing nanodevice on TSMC 0.35 μm silicon chip is shown above.

Fig. 4.10 The measurement environment setup.

Fig. 4.11 The electrodes under measuring are shown above. Electrodes 1 and 2 have silicon oxide region of 30 μm * 15 μm and 30 μm * 5 μm (width * length) respectively. Both electrodes are connected directly to pads without connection with CMOS sensing circuits.

Fig. 4.12 The SEM images of electrodes after labeling Au NPs and after labeling CdSe NPs + Au NPs + CdSe NPs + Au NPs are shown above. The two electrodes in this measurement have the same nanostructure in SEM images due to the same fabrication process. Because the electrodes are too large to be included in the image, we show only the edges parts of electrodes.

Fig. 4.13 The reflective UV-visible absorbance spectrum of nanodevice with structure CdSe + Au +CdSe + Au NPs on silicon oxide substrate is shown above, where the clean silicon oxide was used as blank.

Fig. 4.14 The I-V curves of the photo-sensing nanodevice on Electrodes 1 and 2 when in dark or illumination with 375 nm laser diode. The black line (I_{dark}) means the measuring under dark environment and the blue line ($I_{illumination}$) means measuring under illumination of 375 nm laser diode.

TABLE FOR FULL TEXT OF CHEMICAL REAGENTS

Simplified Form	Full Text (or Synonyms)	Formula	Molecular Weight
APTES	3-aminopropyltriethoxysilane	$C_9H_{23}NO_3Si$	221.37
Cyanamide	Carbodiimide	CH_2N_2	42.04
Citric acid Monohydrate	Acidum citricum monohydricum	$C_6H_8O_7 \cdot H_2O$	210.14
DTNB	5,5'-Dithiobis(2-nitrobenzoic acid)	$C_{14}H_8N_2O_8S_2$	396.35
DTT	dithiothreitol	$C_4H_{10}O_2S_2$	154.2
Hydrogen tetrachloroaurate	Hydrogen tetrachloroaurate(III)	$HAuCl_4 \cdot 3H_2O$	393.83
MUA	11-mercaptoundecanoic acid	$C_{11}H_{22}O_2S$	218.36
NHS	1-Hydroxy-2,5-pyrrolidinedione	$C_4H_5NO_3$	115.09
Tyramine	4-(2-Aminoethyl)phenol	$C_8H_{11}NO$	137.18
TMSPED	N-[3-(trimethoxysilyl)propyl]-ethylene diamine	$C_8H_{22}N_2O_3Si$	222.36