NANOFABRICATION OF INORGANIC FUNCTIONAL STRUCTURES BY PROTEIN SUPRAMOELCUELS WET-NANOTECHNOLOGY

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Introduction

The assessment of the proteins from the nanotechnology and nano-electronics points of view reveals that proteins are ideal nano-blocks for fabricating inorganic functional nano-structures. First, most of protein molecules have the same structure down to atomic scale. Secondly, they can self-assemble to form functional nano-structures. Thirdly, some protein has the surface so designed to selectively sequester inorganic materials (biomineralization) and recent research made it possible to biomineralize metal complexes and semiconductor materials. Lastly proteins are vulnerable compared to the inorganic material which makes it possible to eliminate protein portion of the complex of protein and inorganic material.

Taking advantages of these four characteristics, I proposed making inorganic nanostructures by proteins, the Bio Nano Process (BNP) (1). Namely, utilizing the protein cavity as a spatially restricted biomineralization space, nanoparticle (NP) or nanowire (NW) with identical size is produced and proteins accommodating NP/NW self-assemble into hetero nanostructure of protein with NP/NW on the silicon substrate. After selective elimination of protein portion of the hetero nanostructures, nanometric inorganic structures will be obtained. The appropriate designing of this process can produce inorganic structures with nanometric accuracy. To consolidate the foundation of the BNP, basic research has been conducted.

Biomineralization and nanostructure fabrication

We employed cage-shaped protein, apoferritin to synthesize several kinds of NPs. The structure of apoferritin was solved by X-ray crystallography (Fig. 1) The protein shell is composed of 24 subunits and the outer and inner diameters are 12 nm and 7 nm, respectively. There are narrow hydrophilic and hydrophobic channels connecting the outside and inner cavity. We have successfully introduced source ions through the hydrophilic channels and synthesized Fe-, Ni- and Cr-hydroxide, In-oxide, Co_3O_4, CdSe, CdS, ZnSe, ZnS, Au_2S and several other compound semiconductors (for example see reference 2,3). Fig. 2 shows aurothioglucose-stained TEM images of synthesized CdSe NPs (4).

To use NPs as nanoelectric device components, the placement of NPs was controlled. Genetically modifying the outer surface of apoferritin with short peptides with specific affinity to the carbonaceous surface, we have succeeded to control the protein-protein and protein-substrate interactions so that apoferritin self-assemble into hexagonally close-packed array directly on silicon substrate (Fig. 3). We also demonstrated that mutant ferritin with target specific peptides can be selectively placed on the patterned area (5). Another method which utilizes electrostatic interaction with nanometeric accuracy was developed to place single ferritin onto the positively charged disk (ϕ15nm) made on the Si substrate (6).

The protein portion of ferritin molecule or array was proven to be selectively eliminated by heat- or UV/Ozone-treatment (7). The elimination was confirmed by AFM, FTIR and XPS. The position of the NPs without protein shell observed before and after heat-treatment using high resolution SEM indicated that their positions did not change throughout the heat-treatment and there were no aggregations of NPs.

Making Floating Nanodot-Gate Memory (FNGM) Using Apoferritin

A monolayer of Co-NPs was made on the 3 nm tunnel SiO_2 layer just above the MOSFET n-channel by apoferritin. The protein shell was eliminated and Co-NP array was embedded in the control SiO_2 layer (FNGM, Fig. 4). The high density monolayer of Co-NPs functioned as

floating nanodot gate electrode and the I_D-V_G curves (Drain current – Gate voltage) measured with sweeping gate voltage ±10V, showed a clear hysteresis (8). (Fig. 5). With the narrow gate voltage sweep, the intact MOS I_D-V_G curve was obtained. The hysteresis showed the bi-directional shift of I_D-V_G curve which indicated the electron and hole charging to the embedded Co-NPs. Charge retention characteristic of Co-NPs embedded MOSFET retained good memory window width after 10^4 sec. The endurance of the FNGM up to 10^5 times was confirmed. This result was the same with the Fe-NP embedded FNGM.

Conclusion

We experimentally demonstrated that proteins can make functional inorganic nanostructures in the semiconductor device for the first time through the FNGM prototype production. (8). In the next stage, the BNP will introduce artificial protein and chemical modification of bio-molecules to expand the range of production. As the first try, we are now designing and making large-scale artificial protein supra molecules which will be the template for the fabrication of nanoelectric devices (9). The BNP proposed by our group will open up a new biological path to the fabrication of nano-chips.

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References:

[1] I. Yamashita, *Thin Solid Films*. **393** (2001) 12-18, [2] K. Iwahori, K. Yoshizawa, M. Muraoka, I. Yamashita, *Inorg Chem* ,**44** (2005) 6393-6400. [3] R. Tsukamoto, K. Iwahori, M. Muraoka, I. Yamashita, *Bull. Chem. Soc. J.*, **78** (2005) 2075-2081, [4] I. Yamashita, J. Hayashi, M. Hara, *Chem. Lett.* **33**, (2004) 1158-1159, [5] I. Yamashita, H. Kirimura, M. Okuda, K. Nishio, K. Sano, K. Shiba, T. Hayashi, M. Hara, Y. Mishima, *Small*, **2** (2006) 1148-1152, [6] S. Kumagai, S. Yoshii, K. Yamada, N. Matsukawa, I. Fujiwara, K. Iwahori, I. Yamashita, *Appl. Phys. Lett.* **88**, (2006) 153103-153105, [7] S. Yoshii, K. Yamada, N. Matsukawa, I. Yamashita, *Jpn. J. Appl. Phys*, **44** (2005) 1518-1523, [8] A. Miura, T. Hikono, T. Matsumura, H. Yano, T. Hatayama, Y. Uraoka, T. Fuyuki, S. Yoshii, I. Yamashita, *Jpn. J. Appl Phys*, **45** (2006) L1-L3, [9] K. Sugimoto, S. Kanamaru, K. Iwasaki, F. Arisaka, I. Yamashita, *Angw. Chem. Int. Edi*, **45** (2006) 2725-2728

Figures:

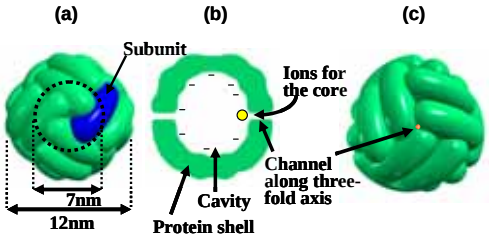

Fig.1 Schematic drawings of apoferritin molecule, (a) looking down along four fold axis (b) cross-section of apoferritin (c) looking down along three fold axis.

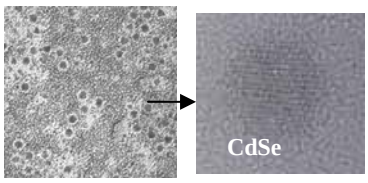

Fig.2 TEM images of CdSe NPs synthesized in the apoferritin cavity. The sample was negatively stained by aurothioglucose which does not stain the cavity.

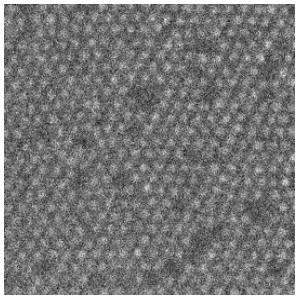

Fig.3 2D hexagonally close packed array of mutant ferritin with NP core directly formed on the Si substrate.

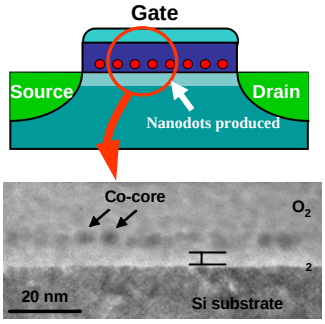

Fig.4 Schematic drawing of cross-section of bio-nanocore embedded n-channel FNGM and the real cross-sectional TEM image.

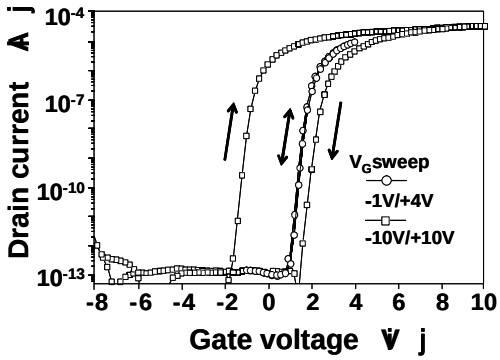

Fig.5 I_D-V_G characteristics of FNGM with the embedded Co-NPs which were synthesized and arrayed by apoferritins.