A new approach to molecular devices using SAMs, LSMCD and Cat-CVD

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Abstract

This paper proposes a new technology for the fabrication of molecular devices using nanotechnology based on liquid and surface sciences recently developed, such as the direct patterning of solid surfaces using the difference of hydrophobic and hydrophilic properties of self-assembled mono-layers and self-assembly films of metal nanoparticles, the fine fabrication of films by the method of Liquid Source Misted Chemical Deposition, and the Langmuir–Blodgett self-assembly films. In these liquid-based technologies, various kinds of organic compounds in solutions, including biological systems, can be used as functional materials in molecular devices. In addition, it has been found that the insulating inorganic films obtained by catalytic chemical vapor deposition are quite effective in the protection of molecular devices against water and/or oxygen. We confirm, from the experimental results presented in this report, that this new approach is practically promising in future.

Keywords: Catalytic chemical vapor deposition; Chemical vapor deposition; Liquid source misted chemical deposition; Molecular device; Langmuir–Blodgett film; Self-assembled mono-layer

1. Introduction

Recent progress in nanotechnology has opened new possibilities of applying functional molecular materials to electronic devices, using either an individual molecule \cite{1}, nanotube \cite{2}, self-assembled mono-layers (SAMs) \cite{3, 4}, Langmuir–Blodgett (LB) films \cite{5} or thin nanocrystals. Particularly, the photochemical reaction of SAMs under vacuum ultraviolet (VUV) light irradiation has markedly attracted researchers attention as a promising nanotechnology for the photographic area-selection of various surfaces such as silicon, ITO glass, metals, and oxides \cite{3}, to a level beyond the scope of the current photolithography used in the semiconductor industry. Also, the direct printing of transistors and other electronic circuits, including electro-luminescence devices, has been achieved by the inkjet method to a resolution of tens of microns \cite{6, 7}. In this method, the hydrophobic and hydrophilic properties of the inks are utilized in the formation of thin films of polymers. To expand this technology to smaller-scale region (down to 0.1 \textmu m), Liquid Source Misted Chemical Deposition (LSMCD) has been developed \cite{8}. Our preliminary results indicate that the LSMCD method is quite useful when used in combination with the nanotechnologies mentioned above under the concept of self-assembly of materials in the liquid-to-solid transformation process as will be discussed later.

In this paper, we introduce a new technology that facilitates the production of the fundamental elements of molecular devices such as the area-selection of a silicon surface by photochemical reaction of SAM, the area-selective deposition of nanomaterials LSMCD, the fabrication of mono-layer films by LB method, the formation of functional donor–acceptor pairs consisting of SAMs, and, finally, the fabrication of films with strong resilience to water and/or oxygen by catalytic chemical vapor deposition (Cat-CVD); which has been recently developed for production of high-quality thin films at low substrate temperatures \cite{9}.
Fig. 1. Demonstration of fabrication processes of integrated molecular circuits: (a) area-selection by photochemical reaction of SAM, (b) area-selective deposition of nanomaterials by LSMCD, (c) additional deposition of SAMs by dipping, (d) area-selective deposition of nanomaterials by LSMCD, (e) deposition of air-protection film by Cat-CVD.

Fig. 2. (a) The molecular structure of photosensitive compound 1, (b) reaction mechanism of the compound 1, (c) schematic illustration of photopatterning for the photosensitive SAM.
2. Fundamentals of the fabrication processes

2.1. General process of construction for nanomolecular devices

In Fig. 1, we show a typical example of fabrication processes for producing each element in a surface integrated circuit: (a) micropatterning process of SAMs on a silicon surface by VUV or UV photography, instead of the usual photolithography, (b) exposure of the SAMs to a mist of metal nanoparticles by LSMCD for the formation of thin metal electrodes on a silicon surface, (c) additional deposition of SAMs, (d) second exposure to the mist of functional molecules, which form the charge-transfer interaction with the SAMs deposited in the process (c), and finally (e) deposition of a ceramic insulator film for protection against water and/or oxidation by Cat-CVD. Details of these processes will be discussed in the following sections. Note that, in addition to the above processes, when we produce an electronic element presented in Fig. 10, an upper electrode in the figure has to be additionally deposited.

2.2. Area-selection by photochemical reaction of SAM

SAMs have attracted much attention not only due to fundamental scientific interest but also to usage as a potential technology for microelectronic devices [3].
Recently, Sugimura et al. [4] demonstrated micropatterning of organosilane SAMs on the basis of photography using an excimer lamp radiating VUV light of 172 nm. This photography is generally applicable to micropatterning of organic thin films including alkyl and fluoroalkyl SAMs. However, this decomposition mechanism, due to the required cleavage of strong C–C bonds in the organic molecules, intrinsically requires high energy light such as VUV, which is extremely expensive for institution of the apparatus and not yet common in the present semiconductor industry. A new SAM, which can be decomposed by the irradiation of UV light at a wavelength of 308 nm, has been synthesized.

The synthesized photosensitive molecule 1 for the UV patterning is shown in Fig. 2(a). This molecule includes three characteristic functional groups, that is, a trimethoxy-silyl group, a 2-nitrobenzyl ester group and a trifluoromethyl group. The trimethoxy-silyl group plays the role of connecting to the hydroxyl groups on the Si wafer to form the SAM. The 2-nitrobenzyl ester group is a photoactive site, which is converted into carboxylic acid by UV irradiation according to the reaction mechanism [10] in Fig. 2(b). The trifluoromethyl group forms a hydrophobic surface on the SAM.

Onto the photochemically cleaned Si wafers, SAMs were formed through the CVD process: the cleaned samples were placed, together with a glass beaker filled with the synthesized compound 1, into a Teflon container. The container was sealed with a cap and placed in an oven.

Fig. 3. Photographs of the area-selective deposition using the photosensitive SAM.

Fig. 4. Schematic illustration of metal nanoparticle protected by ligands.

Fig. 5. TEM image of self-assembled Pt nanoparticles with an average diameter of 6.8 nm.
maintained at 150 °C for 12 h. The molecules reacted with the OH groups on the Si wafer surface resulting in the formation of the hydrophobic SAMs.

In Fig. 2(c) a view of the area selective photoreaction using a photomask is shown. When light irradiated the SAMs’ surface, the hydrophobic surface of the trifluoromethyl groups will change to a hydrophilic surface of the carboxyl groups via the mechanism shown in Fig. 2(b). This difference of hydrophobic and hydrophilic properties of the SAM may be used for the area selective deposition of a material as displayed in Fig. 2(c). The partially irradiated SAM, via the photomask, was dipped in a white paint water solution. When the sample was withdrawn from the solution, the solution was deposited in the irradiation area as shown in Fig. 3. It indicates that by the 308 nm photoirradiation that hydrophilic/hydrophobic interfaces are fabricated on the surface of a Si wafer.

2.3. Area-selective deposition of nanomaterials by LSMCD

For fabricating the micropatterns of metals with the area-selective deposition method, the LSMCD of metal nanoparticles on substrates possessing different surface energy areas is quite effective. To be more specific, one can obtain metal micropatterns by adopting LSMCD of a metal nanoparticle aqueous solution onto a substrate with hydrophobic and hydrophilic patterns in the micrometer regime. Moreover, in a hydrophilic area, the fabrication of regularly ordered metal nanoparticles in 2D or 3D spatial configurations, during solvent evaporation would result in micron-scale metal patterns, in which the electrons show either Ohmic or Coulomb blockade behavior, at room temperature, depending on both the particle sizes and interparticle spacings [11–16]. Therefore, the formation of self-assembled metal nanoparticles with a regularly ordered structure is desirable to control the electron behavior in metal micropatterns. Here, using water-soluble Pt nanoparticles as shown in Fig. 4, a typical TEM image of the resultant micropattern is shown in Fig. 5. In Fig. 6, the SEM image of Pt electrodes on a silicon surface obtained by the LSMCD area-selective deposition is presented. Water-soluble Pt nanoparticles were prepared as follows [13]: hexachloroplatinic acid hexahydrate (H₂PtCl₆·6H₂O) was added to a mixture of trisodium citrate aqueous solution and distilled water. Then, the aqueous solution of sodium borohydride (NaBH₄) was added to the solution, and stirred vigorously for 1 h to obtain water-soluble citrate-protected Pt nanoparticles. The resulting Pt nanoparticles have a mean diameter of 1.8 nm with quite a narrow size distribution.

Since it was found, from the TEM observation that the 1.8 nm citrate-protected Pt nanoparticles did not self-assemble on a flat carbon substrate, the formation of...
self-assembled Pt nanoparticles with a regularly ordered structure is not expected at present in hydrophilic areas either. It is interesting to point out that using larger particles [15] or other protective ligands inducing the weak interligand interaction [16] could resolve this problem.

2.4. Fabrication of nanoparticle mono-layer films by LB method

Metal nanoparticles larger than 2 nm can be easily self-assembled in 2D. On the other hand, fabrication of a 2D ordered structure of small nanoparticles (less than 2 nm) is significantly much more difficult. The LB method was applied to fabricate small Au nanoparticles in 2D in a much wider area than that achieved by self-assembled techniques. Furthermore, during LB process, we added alkanedithiol to a chloroform solution of Au nanoparticles protected by dodecanethiol (DT). Such alkanedithiol plays a significant role in cross-linking the ligand by the partial exchange of DTs as shown in Fig. 7, resulting in the formation of a dense mono-layer film of Au nanoparticles with improved mechanical strength. In Fig. 8(b), a typical TEM image of a cross-linking LB film is shown in comparison with that of the protecting film.

3. Formation of functional SAMs

Organic devices constructed by SAMs are attracting a great deal of research interest because the devices have the potential to demonstrate features different from that of their bulk compounds. At the interface of the SAMs and metal surface, as shown in Figs. 9 and 10, anomalous electronic states are formed because the SAMs at the interface directly undergo coulomb interaction with the metal and the n. n. molecules. As discussed latter in detail, the molecules in (a) of Fig. 10 are placed along the specific field formed between two metal surfaces. If the field and the electronic states of the molecules can be controlled, we will fabricate new electronic devices based on these organic compounds. From this viewpoint, molecular devices containing SAMs, which construct a regular mono-layer on a metal surface, are attracting much attention both fundamentally and application wise.

Up to now molecular charge-transfer materials based on donor and acceptor organic systems have been extensively investigated because the complexes show characteristic physical phenomena such as neutral–ionic (NI) phase...
transitions caused by cooperating effects of the coulomb repulsion and the electron–lattice interaction [17]. When the concept of the NI phase transition is applied to the SAMs system as shown in Fig. 10, a new type of the 2D or half-infinite NI phase transitions is expected. Namely, the charge-transfer between the SAMs and the metal surface or the n. n. molecules might occur. This provides many possibilities for construction of molecular devices. As shown in Fig. 10, the NI phase transition induces an electric dipole of donor/acceptor pairs (Fig. 9), which provide a change of the contact potential ($V_c$) between the two metal surfaces. Since the order of $V_c$ is a more or less 1 eV, an extremely high electric field of more than $10^5$ V/cm is induced between the surfaces with a distance of ca. 10 nm. Thus, molecular devices, such as an organic memory device, can be expected to form when the NI transition is controlled optically or by an applied electric field [18,19]. When an electric-field-dependent material is inserted into (a) of Fig. 10, an organic RAM is possible. To begin with, we fabricated and investigate a donor SAM containing a ferrocene unit and its doping layer of Br$_2$.

The thiol mono-layer was formed by soaking gold substrates in ethanol solutions of a ferrocene-terminated thiol (11-Ferrocenyl-1-undecanethiol) at 1 mM. The sample was removed from the adsorption solution after 2 days, and washed in ethanol. Cyclic voltammogram of the Fc-SAM (mono-layer of Fc(CH$_2$)$_{11}$SH on gold) was measured with electrolyte solution of 0.1 M NBu$_4$PF$_6$ in CHCl$_3$. One reversible wave at $E_{1/2} = 0.49$ V, which corresponds to the redox process of the iron center and shifts from 0.40 V of free 11-Ferrocenyl-1-undecanethiol, was observed. In Fig. 11, the spectra of X-ray photoelectron spectroscopy (XPS) of Fe (2p$_{1/2}$, 2p$_{3/2}$) for free 11-Ferrocenyl-1-undecanethiol and Br$_2$ doped Fc-SAM. The position of a photoelectron peak is sensitive to the charge density on the atom. By doping Fc-SAM with Br$_2$, the charge density of the iron ion is largely decreased, because the atoms are oxidized by Br$_2$. Corresponding to the oxidization of Fc-SAM, the change of the $V_c$ was observed to be ca. 0.6 eV [20].

4. Protection of molecular devices by Cat-CVD films

Cat-CVD, often called Hot-Wire CVD, [9,21,22] is a new method to obtain device quality CVD films at low substrate temperatures. In the method, gas molecules are decomposed by catalytic cracking reactions on heated catalyzer placed near substrates (Fig. 12), instead of the

![Fig. 11. XPS spectra of Fe (2p$_{1/2}$, 2p$_{3/2}$) for (a) ferrocene and (b) its Br-doped SAM containing ferrocene on Au films.](image1)

![Fig. 12. Schematic diagram of Cat-CVD and gas-phase dynamics [21].](image2)
plasma decomposition in conventional plasma enhanced CVD (PECVD) [23]. As shown in Fig. 12, the apparatus consists of only three parts, that is, the gas-inlet, substrate holder and catalyzer placed between gas-inlet and substrate holder. Tungsten (W) or tantalum (Ta) wires are commonly used as the catalyzer, and they are spanned in parallel to the substrate holder. So, it is easy to connect the LSMCD to other processing apparatus.

Fig. 13 shows the infrared absorption spectra of Cat-CVD SiN$_x$ films prepared by both PECVD and Cat-CVD, after exposure of the samples at 120 $^\circ$C in 2 atomic pressure water vapor for 96 h. In the case of PECVD films, the Si–O stretching mode comes out after exposure, but it cannot be detected for Cat-CVD films. This demonstrates the large resistivity of the Cat-CVD films against water penetration presumably due to high packing density of films prepared by Cat-CVD method. This also implies the feasible use of Cat-CVD films as passivation films for organic materials such as insulating nanofilms with a high break down voltages.

5. Remarks

In this report, we proposed a new type of fabrication method for molecular devices concentrating our attentions on the control of the interfaces between SAMs and metal surfaces in the nanoscale region through the charge-transfer interaction, which are expected to create new phenomena in the scientific fields of liquid and surface states. In addition, any soluble material can be used in this method, suggesting an easy expansion of the technology presently proposed to the field of biotechnology [24], which will allow us to study biological materials electro-chemically in the nanometer scale.

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Fig. 13. Infrared absorption spectra of Cat-CVD films prepared by PECVD (fine line) and Cat-CVD (heavy line): an arrow shows the Si–O stretching mode.
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