

# Nanoscale Surface Architecture Laboratory

Department of Materials Science and Engineering  
Kyoto University

*Fabrication of functional materials based on the surface architecture through assembling molecules, atoms and other nanoscopic objects.*

Materials emerge much more effective functions when proper shapes and microstructures have been provided. Furthermore, by precisely locating such functional material units, a novel function can be constructed through the cooperative harmonic action between the functional units. We have continued the research on science and technology of "**nanoscopic surface architecture**" in order to fabricate, assemble and integrate materials into a regulated structure in the minute scale down to the atomic/molecular level. Our interests are currently focused on thin films and surfaces consisting of organic molecules and organic-inorganic interfaces.

## Research Subject 1:

*Organic and organic-inorganic thin films fabricated by self-assembly*

"**Self-assemble**" is a process by which molecules spontaneously assembled and well-organized into a material. Self-assembling occurs during some types of chemisorption due to interactions between adsorbing molecules and a substrate (Fig. 1-1). We have been studying on fabrication of organic monolayers and organic-inorganic multilayers in which each layer is controlled to be a monomolecular thickness.

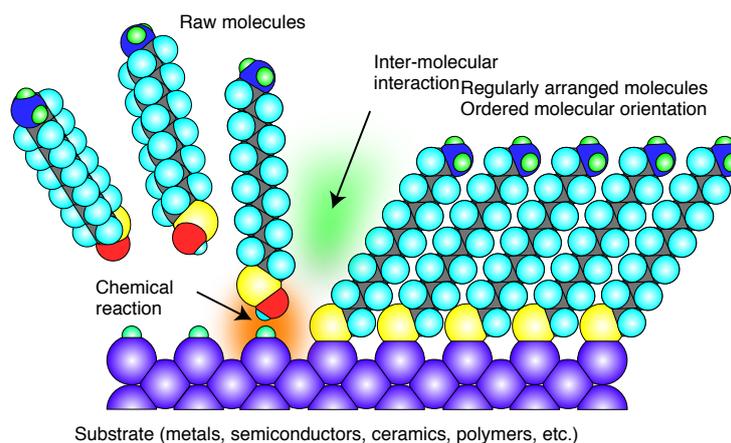


Fig. 1-1 **Self-assembled monolayer.**

## *Attachment of organic molecules onto a semiconductor surface through chemical processes*

We have been studying on the process for immobilizing organic molecules onto silicon surfaces and chemical/physical properties of such **organic-semiconductor interfaces**. Organic molecules, for example, unsaturated hydrocarbons, aromatic compounds, alcohols and so forth, react with hydrogen-terminated silicon surface and, consequently, attach covalently to the surface. We expect that this material becomes a new electronic material, as well as its usefulness in a fundamental scientific research on the electron transfer between silicon and organic molecule.

When a molecule containing a carbon-carbon triple bond reacts with a hydrogen-terminated Si surface, a SAM with an interfacial structure of  $\equiv\text{Si}-\text{CH}_2=\text{CH}_2-$  is formed as shown in Fig. 1-2. A current-voltage (I-V) characteristic of a junction between this  $\pi$ -conjugated SAM/Si sample and a gold-coated AFM probe was compared with that of a Si(111)-H surface. The contact resistance between Au and  **$\pi$ -conjugated SAM** is lower than that between Au and Si-H. Electrical properties of Si surfaces can be controlled by preparing a directly-bonding SAM on the surfaces.

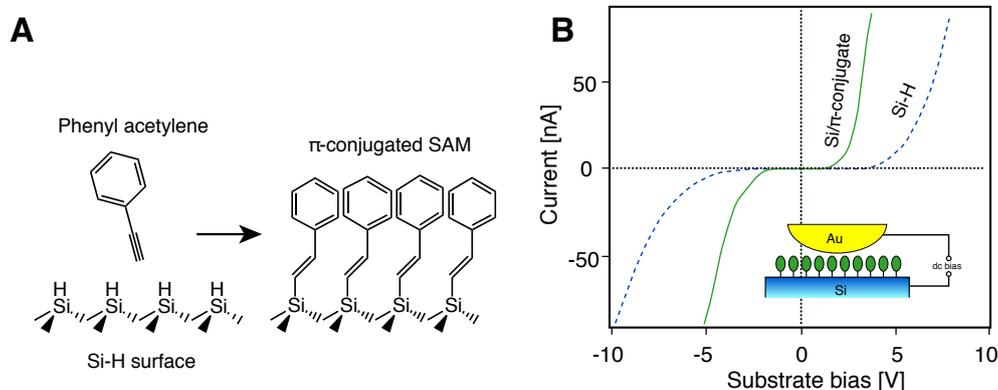


Fig. 1-2  **$\pi$ -conjugated monolayer**. A) SAM on Si prepared from phenylacetylene. B) I-V characteristics of the junctions formed under an Au-coated AFM probe with the SAM-covered Si or Si-H surfaces.

**Redox-active** molecules have an ability to store and release electric charges reversibly. SAMs of such redox-active molecules attached to silicon are, thus, expected to be applied to solid-state memory devices. Vinylferrocene (VFC) and ferrocenecarboxaldehyde (FCA) molecules were attached to a Si(111) surface through Si-C and Si-O-C bonds, respectively, as shown in Fig.2-2. Clear oxidation and reduction peaks are observed in cyclic voltammogram of the samples. Redox activities were successfully built in the Si substrate.

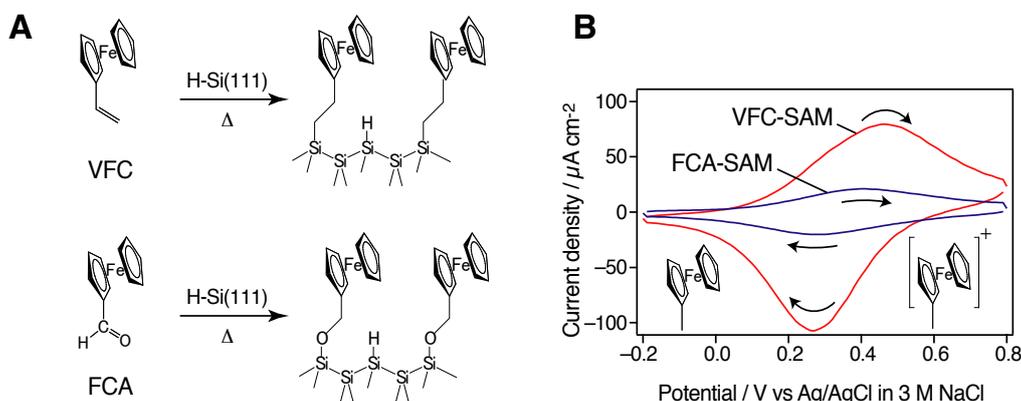


Fig. 1-3 **Redox-active monolayer**. A) Thermal reaction of vinylferrocene (VFC) or ferrocenecarboxaldehyde (FCA) molecules on hydrogen-terminated Si surfaces. B) Cyclic-voltammogram of VFC- and FCA-immobilized Si electrodes.

### Self-assembled multilayer formation through metal ion-organic acid complexation

A **self-assembled multilayer** consisting of transition metal and biscalboxyl acid has been fabricated by simply immersing an oxide-covered silicon substrate into zirconium (Zr) n-butoxide and telephthalic acid (TPA) solutions alternately. In this multilayer, two TPA monolayers were bridged with a Zr(IV) monolayer. The chemistry connecting these monolayers is most likely **coordinate bonds** between Zr(IV) ions and carboxyl groups. Besides Zr, Ti has been proved to serve as a bridging layer as well. This method is promising since a wide variety of organic biscalboxyl molecules are applicable in order to design novel functions of the multilayer.

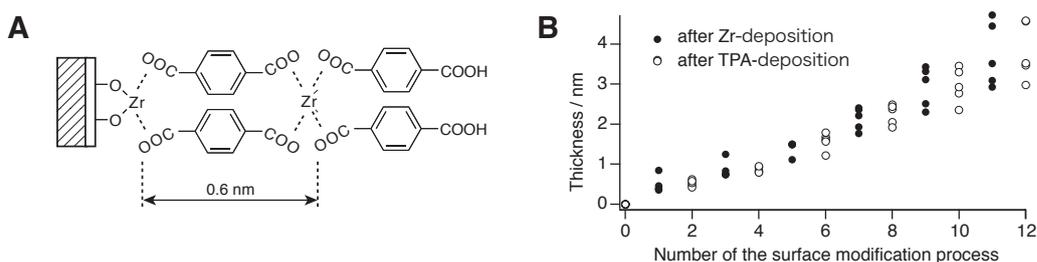


Fig. 1-4 **Alternate Stacking of Zirconium and Telephthalic Acid Layers**. A) Schematic illustration of the growth behavior of Zr-TPA self-assembled multilayer, B) Thicknesses of layers grown on oxide-covered Si substrates by alternately conducted Zr-process and TPA process.

## Research Subject 2:

### Micro - nano fabrication based on self-assembled monolayer lithography

Our research is focused on application of self-assembled monolayer (SAM) in micro-nano fabrication technologies. Minute objects, that is, nano-particles, nano-crystals, free-spaces, etc., have been spatially arranged on solid substrates with an intentionally designable pattern. Such a pattern was first fabricated on substrates covered with a SAM using a lithographic method, for example, photolithography, energy-beam lithography or scanning probe lithography and, then, modified through a surface modification process in order to provide a proper chemical affinity to nano-objects. The nano-objects were chemically manipulated by using the fabricated pattern as a template.

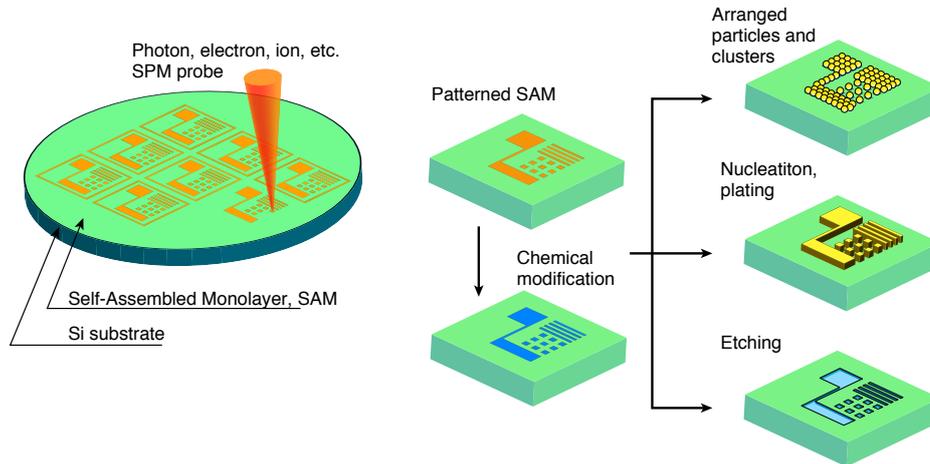


Fig. 2-1 **Programmed assembling** of minute objects based on SAM lithography.

### VUV microfabrication

**Vacuum ultra-violet** (VUV) light at 172 nm in wavelength is applied to microprocessing of organic materials including polymers and SAMs. The VUV light can generate atomic oxygen species, which have strong oxidative reactivities, through excitation of atmospheric oxygen molecules. This is the crucial advantage of our **VUV microprocessing technology**, since any organic material surfaces can be modified with atomic oxygen species and, consequently, be micropatterned even if a sample material has no photoreactivity. Namely, VUV photoprocesses are **chemically amplified with atomic oxygen**.

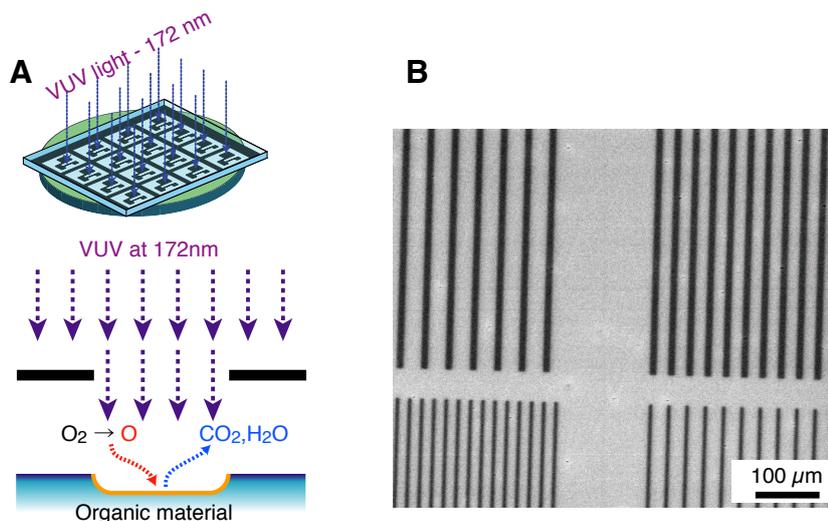


FIG.2-2 **VUV-microfabrication**. A) Photochemical modification of an organic material surface. Oxidation and/or etching amplified with atomic oxygen species. B) FE-SEM image of a VUV-patterned alkyl SAM on Si. The dark region corresponds to the VUV-irradiated area. At present, 0.5  $\mu\text{m}$  lines have been successfully printed.

## Manipulation of molecules and chemical reactions based on scanning probe microscopy

Scanning probe microscopy (SPM) has an aspect as nanofabrication tools. We have explored nanofabrication processes based on chemical reactions locally induced with an SPM probe, that is, “**nanoprobe chemical conversion**”. We have succeeded in oxidizing and reducing solid surfaces at a resolution close to 10 nm. By integrating this nanoprobe chemical conversion and other surface finishing technologies, a variety of materials ranging from metals to polymers can be assembled on a substrate surface in nm scale.

As schematically illustrated in Fig. 2-3A, a material surface is modified with a sharp SPM tip with applying a bias voltage between the tip and the substrate. For example, a SAM/Si was electrochemically oxidized at the tip-contacting point resulting in the formation of a protruded mound consisting of silicon oxide (Fig. 2-3B). Figure 2-3C shows an Au nano-dot array obtained by an integrated process in which the nanoprobe chemical conversion, wet etching and electroless plating were combined.

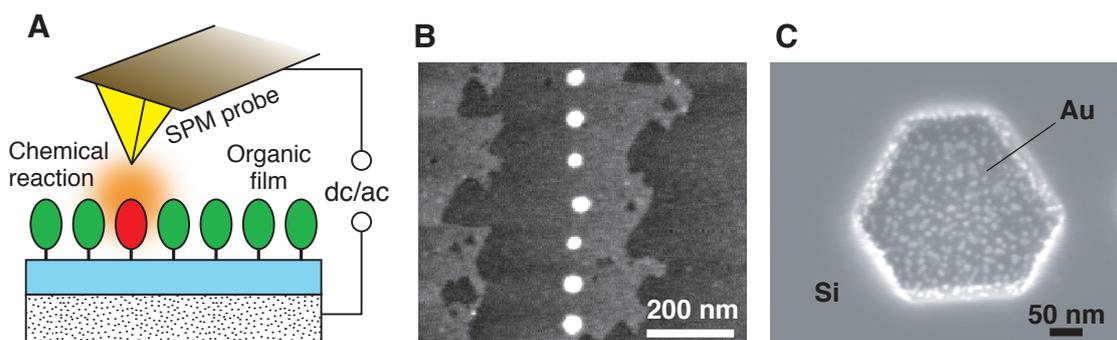


Fig. 2-3 **Nanoprobe chemical conversion.** A) Schematic illustration of SPM- based chemical conversion, B) Topographic image of anodized dots formed on a SAM-Si surface, and C) FE-SEM image of an Au nano-dot array consisting of Au nano-dots around 10 nm in size located at the bottom of an hexagonal hole.

## Spatial arrangement of gold nanoparticles on to micro-nano templates consisting of SAMs

Gold (Au) nanoparticles are spatially arranged on particular regions on micro - nanotemplates through acid-base interaction. The templates are prepared by VUV microfabrication or nanoprobe lithography. There are two types of processes for Au nanoparticle assembly. One is a positive tone process (A): First, micro or nanopatterns are fabricated on an alkyl SAM covered substrate (Si, SiO<sub>2</sub>, ITO etc.). Next, an aminosilane SAM is backfilled into the area where the alkyl SAM has been removed. Through an attractive interaction between citrate (acid) capped Au nanoparticles - negatively charged and the amino(base)-silane SAM surface - positively charged, the Au nanoparticles are self-aligned onto the amino-terminated surface. The other is a negative tone process (B): In this process, particularly applied to SiO<sub>2</sub> substrate, an aminosilane SAM formed on a substrate is micropatterned so that the substrate SiO<sub>2</sub> surface is exposed. Since, the amino-terminated surface is positively charged while the exposed SiO<sub>2</sub> surface is negatively charged, Au nanoparticles are area-selectively assembled onto the remained aminosilane SAM surface.

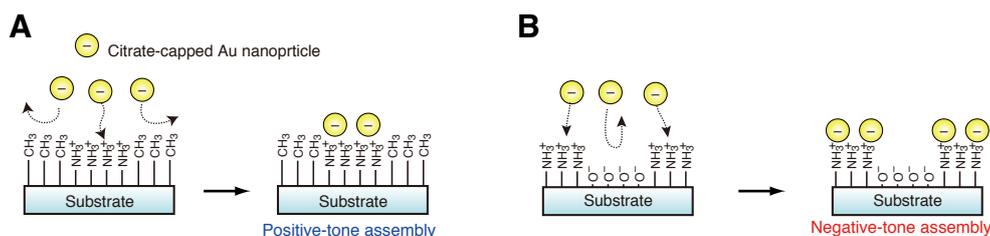


FIG.2-4(A, B) **Gold nanoparticle arrays**  
A) Positive tone process. B) Negative tone process.

(C): FE-SEM image demonstrating that Au nanoparticles are confined on lines of  $0.5 \mu\text{m}$  in width. This Au nanoparticle array was fabricated on Si by the positive tone process. The line pattern was printed on an alkyl SAM/Si by VUV microfabrication. (D): AFM image showing Au nanoparticles are aligned on sub- $\mu\text{m}$  wide lines. This Au nanoparticle array was fabricated on  $\text{SiO}_2$  by the negative tone process. The line pattern was printed on an aminosilane SAM/ $\text{SiO}_2$  by VUV microfabrication. (E): FE-SEM image of Au nanoparticle lines with a single nanoparticle width fabricated on Si. The lines near  $10 \text{ nm}$  in width were drawn on an alkyl SAM/Si by nanoprobe lithography.

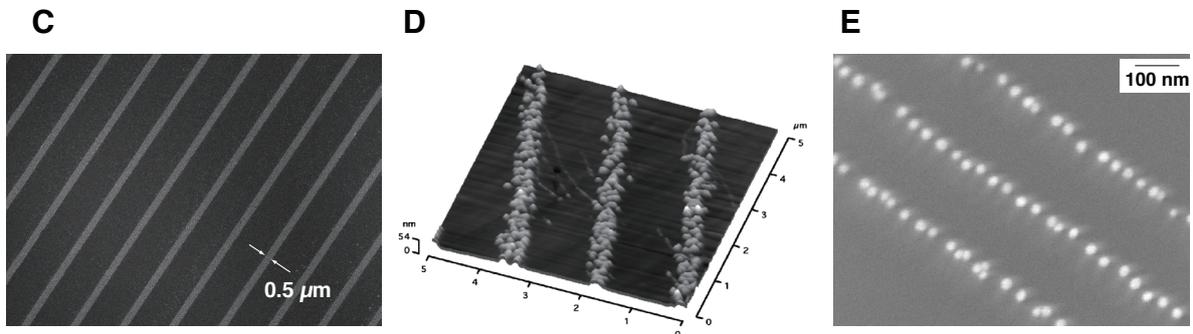


Fig. 2-4(C, D, E) Au nanoparticle arrays C) fabricated on Si by the positive tone process based on VUV microfabrication, B) fabricated on  $\text{SiO}_2$  by the negative tone process based on VUV microfabrication, and D) fabricated on Si by the positive tone process based on nano-probe lithography.

### Research Subject 3: High-resolution atomic force microscopy at liquid-solid interfaces

Observation of material surfaces at an atomic/molecular resolution is of special interest in order to understand surface chemical/physical processes proceeding at a solid-liquid interface. We have developed a frequency modulation atomic force microscope (**FM-AFM**) system which can be operated in liquid or solution, even in an ionic liquid. The system uses a quartz tuning fork sensor working in a high viscosity media.

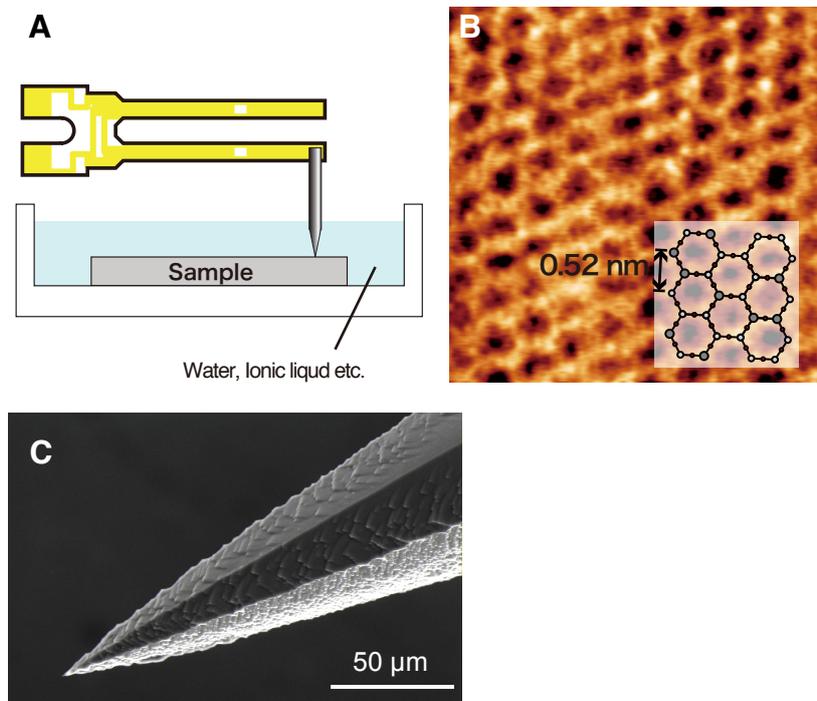


Fig. 3-1 **Atomic force microscopy in a high viscosity liquid.** A) FM-AFM system using a quartz tuning fork sensor. B) An atomically resolved image of a mica surface immersed in an ionic liquid. The characteristic honeycomb feature of mica surface is clearly acquired by our AFM system. C) A stylus made of Si for right-weight AFM probe to obtain a higher Q-factor.

## Research Subject 4: VUV photochemical processing

### Photo-activation bonding of polymeric materials

A new adhesive-less bonding technology for resin plates, that is, **photo-activation bonding**, has been developed and successfully applied to bonding and sealing processes for all-resin micro-fluidic plates. This technology is based on the photochemical activation process, in which vacuum ultra-violet light (VUV) is used for surface modification of the resin surfaces.

When a resin surface is irradiated with VUV light at 172 nm in wavelength under an atmosphere containing oxygen molecules, both the resin surface and the atmospheric oxygen molecules are excited. Consequently, photochemical reactions are induced at the surface resulting in the formation of a chemically active layer consisting of oxidized resin molecules with a lowered molecular weight and bearing hydrophilic functional groups, such as  $-\text{COOH}$  and  $-\text{CHO}$ . The photo-activated resin plates can be bonded by using the activated layers on them as glue. Among various resins, we have focused on surface activation and bonding of optically transparent resins, that is, cyclo-olefine polymer (COP), polymethylmethacrylate (PMMA), polycarbonate (PC) and polyethylene (PE). These resins have been successfully bonded by the photo-activation bonding. Plates made of different resins could be bonded as well.

We actually fabricated micro-fluidic plates made of COP and confirmed their performance. The photo-activation bonding has been proved as the practical method for bonding and sealing of the all-resin plates. In addition, the photo-activation bonding was found to have a particular advantage that the low-fluorescent property of COP was not seriously degraded. By combining a fluorescence reduction technique we have developed, low-fluorescent COP plates comparable to glass-made plates can be fabricated.

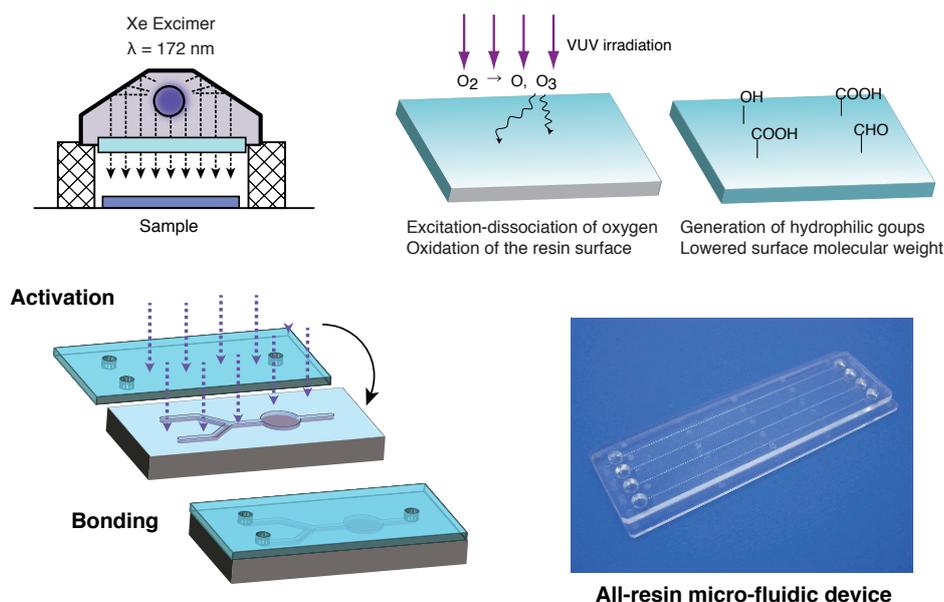


Fig. 4-1. **Photo-activation bonding** of resin plates using VUV light.

### VUV-induced oxygen-trimming from graphene oxide

Graphene is a well-known 2D material showing unique properties. A oxidized graphene so-called graphene oxide (GO), a chemical derivative of graphene, can be readily produced by a low cost process based on oxidation and delamination of graphite. Since GO is bearing with polar functional groups such as  $-\text{OH}$ ,  $\text{COOH}$ , etc., it is dispersible in various solvents including water. Consequently, GO nanosheets can be readily delivered on a solid substrate through a simple solution method, e.g. spin-casting. Applications of GO are thus expected. However, electrical properties of GO are degraded compared with graphene so that their recovery is highly required for practical applications of GO.

We have found that oxygen-containing parts were removed from GO with VUV irradiation in vacuum so that reduced GO (rGO) was formed. This VUV-rGO was much more conductive than GO. This selective cleavage of C-O bonds in GO is called as “oxygen trimming”. Furthermore, Kelvin-probe force microscopy (KFM) was proved to be a powerful means to identify the reduction degree of VUV-rGO through the surface potential change due to “oxygen trimming”.

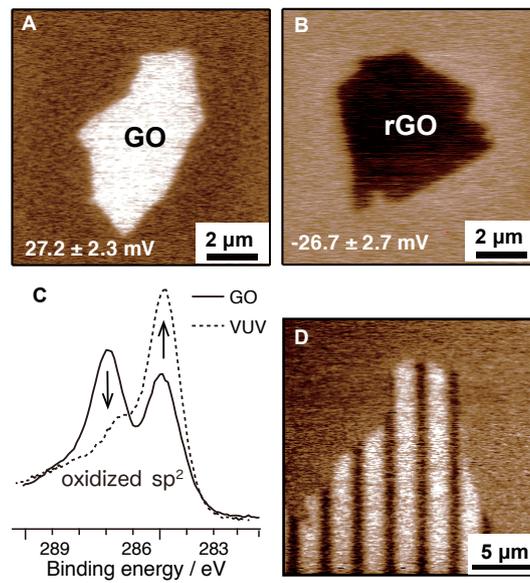


Fig. 4-2. Reduction of GO by VUV-induced oxygen trimming. A) KFM image of a GO sheet which showed a higher surface potential than a substrate Si. B) KFM image of a VUV-reduced GO sheet. This rGO showed a lower surface potential than the Si substrate. C) C1s-XPS profiles of GO and VUV-rGO. Due to the VUV irradiation, the oxidized part in GO reduced, while its  $sp^2$  carbon part increased. D) rGO microlines fabricated in GO VUV-irradiation through a photomask. This method might be applicable to draw rGO/GO circuit patterns with sub- $\mu\text{m}$  resolution.

#### Staff

**Professor:** SUGIMURA, Hiroyuki; 杉村 博之

**Assistant Professor:** ICHII, Takashi; 一井 崇

**Assistant Professor:** UTSUNOMIYA, Toru; 宇都宮 徹