Guest Forum

The Screening Committee Lecture for the First Dr. Masao Horiba's Award

Deployment of Electrochemical Nanotechnology

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Described in this article are examples of research and development for manufacturing devices and materials in the nanotechnology field based on electrochemical methods. Additionally, there is an introduction concerning HORIBA's activity to configuring biosensing devices. These devices combine electrochemical nanotechnology with FET technology.

Background and Motivation for Research

Electrochemistry

The principal area of interest of electrochemistry is in the electrically conducting metal electrode and the solution that contacts this electrode. Here, the most important factor determining deposition and reaction is the electric double layer[*1], therefore, a key point is how to control the layer, which essentially acts as a barrier. Water has an extremely high dielectric constant, approximately 80, so if the surface of an electrode is positively or negatively charged (normally negatively), a dielectric layer is created in which the water molecules will be well aligned. This is the so-called electric double layer, and it acts as a barrier to the progress of a reaction. Therefore, almost all electrode reactions are regulated resulting from how this area has been implemented. For example, if positive metal ions approach the interface of an electrode, metal is deposited when electrons react across the barrier layer, because the ions cannot enter the barrier layer. Consider this as the electrochemical model of the interface. It is important to appreciate how such a thin layer so profoundly influences the electrochemical reaction.

*1: This is an "electrical dipole," which can be described as follows: A positive electric charge is continuously distributed on one side of a surface, and a negative electric charge is continuously distributed on the other side of the same surface. The positive and negative electric charges are extremely close, and their field densities are equal.

Controlling Interface

One of the controlling methods for the interface layer is to use unique adsorption species that change the state of the electric charge of the interface by breaking into the dielectric layer of water. In many cases these unique adsorption species are anions, but the reaction of the electrode varies enormously depending on what kind of unique adsorption species is used. The most interesting among them are adsorbed atoms known as ad-atoms or simply adatoms, which have recently become the center of attention in many research areas. For example, how to control a reaction field by interfering or accelerating the reaction between positive metal ions and electrons. In other words, the adsorbed atom below a monatomic layer generated at the interface, known as an adatom, substantially changes the reaction process, and this change induces various phenomena. Figure 1 shows the outline of a deposition reaction in the presence of adatoms.

A fundamental idea in our laboratory is that we aim to create a thin film that cannot be created by the usual electrodeposition means by controlling the interface using such adatoms. Thus when performing research, it is a prime motivation to seek methods to create advanced and functional substances by utilizing advanced amorphous composition control. This will result in generating materials that have unique structure or unique functional interfaces.

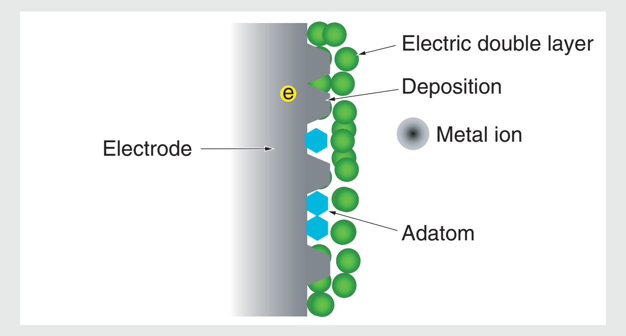


Figure 1 Adatom and Deposition Reaction

The Influence of Adatoms - Basic Magnetic Disk Research

The first example application of the basic idea of using adatoms as control was in the manufacture of 8-inch plated disks for a 400 MB small magnetic disk, which was released by Nippon Telegraph and Telephone Public Corporation in 1981.

Research for plating disks for practical use had been progressing for several years in some companies at that time, but even if chemical constituents of high purity and clean water were used, the coercive force of the created plating medium was different every time. Therefore, it was very difficult to put into practical use. To cope with this problem, the manufacturer requested our university to do this research, as they wanted the problem solved quickly. However, from the idea of the late Professor Yoshida, (who was my predecessor's professor) that the university should perform fundamental research, we started joint research under the assumption that we would rather perform fundamental research over a long period. We hypothesized that the reaction at the interface was changed by impurities below a monatomic layer of the heavy metal and researched metals that may control the interface as the adatom. As a result, we came to observe that the coercive force was reduced to 30% when 100 ppm of iron ions were injected into the plating solution. There are approximately 10 ppm of impurities in the cobalt chemical used for the cobalt alloy plating even if it is high purity. Then, we designated the limitation for the impurities mixed in the chemical solution, especially the amount of iron ions, and succeeded in stabilizing the coercive force of the plating medium. Additionally, we found that the size of cobalt particles was essentially changed by iron to improve the coercive force. At present, such adatoms can be clearly distinguished by scanning tunnel microscope (if a solution-based type is used). Now we can prove the facts that were guessed from our numerous experiments in those days.

Advanced Functional Paddle Cell and Filter System

When IBM developed a thin film head in 1979, the idea called the paddle cell system was proposed for permalloy plating. The idea is to finely agitate the part to be plated with a turbulent flow at a distance of approximately 1 mm, resulting in a very uniform reaction. As electrodeposition generates hydrogen at the same time to reduce hydrogen ions, the pH value of the minute area at the interface changes as time passes. If the pH value changes, the deposition composition of the permalloy NiFe changes, therefore, change of the pH value is controlled by intense agitation to maintain the deposition composition at a constant level. In permalloy plating, the composition ratio of iron and nickel must be controlled to an accuracy of 0.1% to satisfy the required characteristics. This is possible using the paddle cell system. In our laboratory, we use the vertical paddle cell system to facilitate this.

We proposed using a Teflon based filter system to obtain water of high purity at a time before such water was needed for semiconductor manufacture, a method in common use now. In those days we could not get this filter in Japan, so we had to get it from overseas. In the end, a filter system made from 0.2 µm Teflon (normally two steps) was installed outside the tank in the clean room, then accurate fine patterns for electronics could be created. Figure 2 shows a configuration example of the paddle cell system and filter system. Thus we started some research in the electrochemistry field and have continued up to now with two technologies regarded as important in fine-pattern film forming techniques.

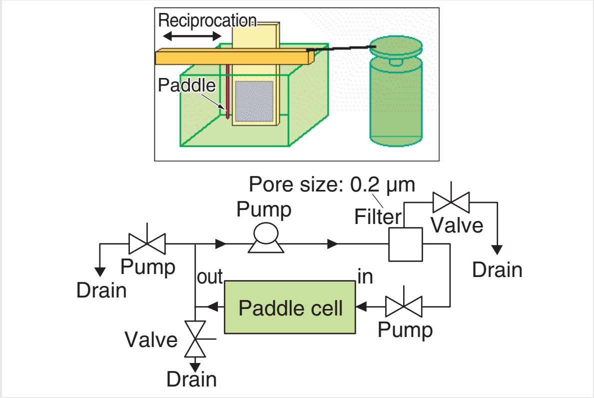


Figure 2 Paddle Cell and Filter System

Application Example of Electrochemical Nanotechnology

Magnetic Thin Films for Magnetic Recording Devices

Recent Development of Magnetic Recording

The storage density of the magnetic disk has been improved 100% or more annually since 1997, but it has reduced to about 30% since 2002 and 2003 (Figure 3). Heads are categorized into reading types and writing types, and read heads are manufactured using a spattering method. For write heads, plating is used for almost all industrialized processes, because there is an advantage that with the paddle cell system, the film thickness does not change even at the points where there are large shape changes, such as step-shaped areas. In this field, materials having a high saturation magnetic flux density (Bs) and low coercive force are required, and permalloy (Bs 1T (Tesla)) $Ni_{80}Fe_{20}$, 1.6 T $Ni_{45}Fe_{55}$) has been used, but they have been replaced since 2001 by CoNiFe[*2] of Bs 2.1 T as we have proposed. Now we propose the CoFe of 2.4 T plating film which has a higher Bs. The other hand, Co/Pd multilayer film and FePt-based film using the spattering method have been proposed for recording media, and it has been said that there will be a shift to the pattern system[*3] for the next generation of recording media.

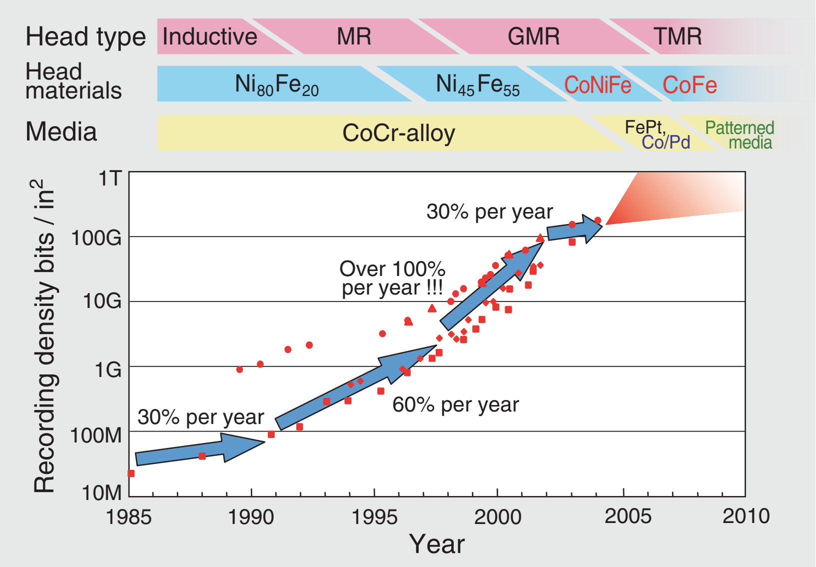


Figure 3 Recent Developments in Magnetic Recording

The MR (Magneto-Resistance), GMR (Giant Magneto-Resistance), and TMR (Tunneling Magnet-Resistance) heads are read heads that use the phenomena that electrical resistance changes according to magnetic field intensity, and they can become magnetic recording heads by combining this technique with inductive heads (electromagnetic induction type heads).

[*2] CoNiFe plating was jointly developed by Professor Tetsuya Osaka of Waseda University, Applied Engineering and NEC, and the patent income of Waseda University, Technology Licensing Organization went up to 200 million yen.

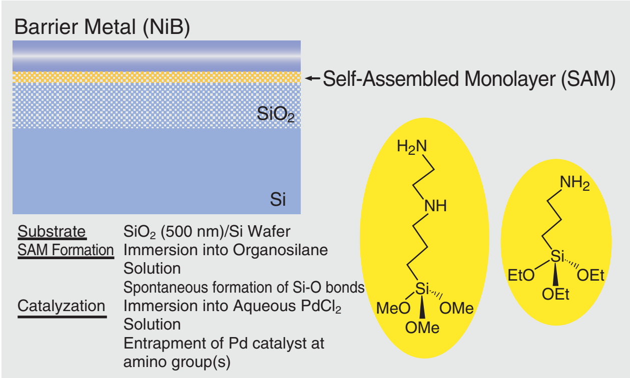
[*3] This is a "Nano-structure magnetic body" arranged on a substrate with the crystal axes of the magnetic particles aligned.

CoNiFe Film

A film has been sought that has the three desirable characteristics of high-saturation magnetic flux density (Bs), low coercive force, and mechanical flexibility. The CoNiFe film that we developed attains Bs 2.1 T. This was possible by controlling the levels of impurities. In fact, saccharin was used as an additive for flattening the plating film. If this was used, sulfur was then deposited at the same time as the additive, and it entered the plating film at 0.3% concentration, largely changing its magnetic properties. On the other hand, we found that reducing the fine amount of sulfur moves the boundary between the face-centered surface and body-centered surface toward higher magnetic flux density. We supposed that particles become fine as the face-centered surface and body-centered surface coexist at this boundary layer. Then the additive that deposited the sulfur was removed, and plating was performed. Namely, the film of fine particles becomes a soft magnetic film. Fortunately particles up to 10 nm in size could flatly adhere without any additive, and so the soft magnetic film of Bs 2.1 T was successfully obtained. The CoNiFe film having a high saturation magnetic flux density of twice that of conventional permalloy film was put in practical use, and the write head was radically miniaturized to 10 μm or less.

VLSI Fully Wet Copper Interconnect Process

IBM developed the Damascene method[*4] in 1997, and interconnect materials were changed from aluminum to copper. As copper has good conductivity, its resistance rises very little even if the interconnect pitch is very fine, and as a rule the operation is performed without problems to under 0.3 μm, therefore this technology is mainstream now. Generally this method is performed as follows; Create a film of tantalum nitride or titanium nitride on the SiO_2 as a barrier layer, apply copper using the spattering method as a seed layer, then perform plating. We propose a process to perform these steps by using the fully wet process. Under this process, we develop the self-assembled monolayer (SAM) having a silanol group and amino group applied on the SiO_2, onto which nickel boron (NiB) is applied by electroless plating as a barrier layer for the copper, and then perform copper plating as is. This method is for fabricating a uniform SAM without surface defects on the SiO_2 (Figure 4). After applying the SAM, the surface is immersed in the $PdCl_2$ solution, Pd is coordination-bonded to the amino group of the SAM, and the monolayer of Pd is created. Pd becomes the catalyst for the electroless plating, and electroless NiB can then be automatically applied. The thickness of NiB is 15 nm, which can work as a barrier layer for stopping the diffusion of copper.



Substrate	SiO_2 (500 nm)/Si Wafer
SAM Formation	Immersion into Organosilane Solution Spontaneous formation of Si-O bonds
Catalyzation	Immersion into Aqueous $PdCl_2$ Solution Entrapment of Pd catalyst at amino group(s)

Figure 4 Fabrication of NiB Barrier Layer on SiO_2

[*4] This is an interconnect forming method where the metal is deposited in the grooves created in the inter-layer insulating film, and the metal outside of the grooves is removed.

Microbiological Sensor

Chirality Sensor

We are researching for a method to detect enantiomers by gold vapor deposition (Au (111)) on a QCM (Quartz Crystal Microbalance) by applying the self-assembled monolayer onto it, which can detect chirality*5. The first interesting data obtained with this method is from the phenylalanine and thalidomide molecule. The group at Hokkaido University realized a two-dimensional chiral arrangement by applying (R)-form or (S)-form monolayer of binaphthothiol (BNSH) to Au (111). This may be used for the sensor because, as shown in Figure 5, the holes (the substrate section of the gold which looks red) are created. They divide in a counterclockwise direction and clockwise direction toward the contacting direction of vertices of the equilateral triangles indicated by six white circles. If this is applied to the QCM, only the (R)-form thalidomide responds to the (R)-form BNSH, while the (S)-form does not respond. On the other hand, only the (S)-form thalidomide responds to the (S)-form BNSH, and the (R)-form does not respond. They are mutually exclusive in selectivity. Since the time until saturation is as long as 100 seconds, we are considering a method to make it faster by combining with a FET.

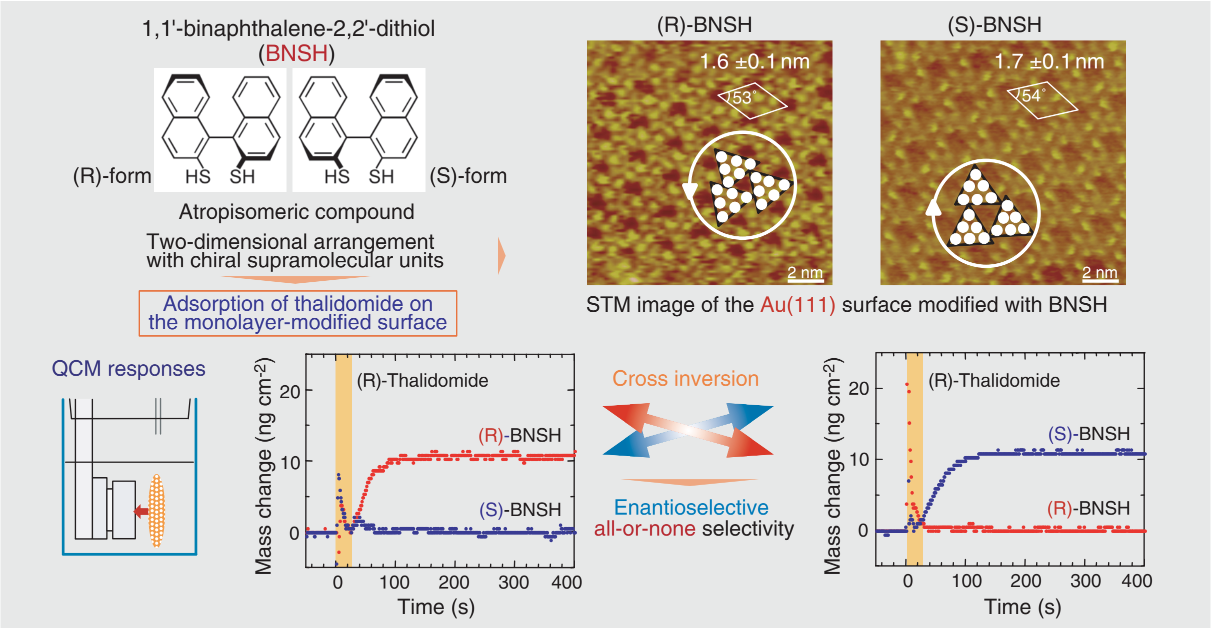


Figure 5 Enantioselective Adsorption on Self-Assembled Monolayers with Two-Dimensional Chiral Arrangement

Microbiological Sensor Applied to a FET

To fabricate the combination of the biological sensor and FET, we planned to fix various parts to the gate as desired, particularly to use a SAM for improving the sensitivity, and additionally to desirably attach the DNA or protein in the desired way. We started from the design of the FET and aimed for the following three points: 1) To create a larger FET than the available commercial FETs to ensure larger current output 2) To establish a fixing process while stabilizing the monolayer. 3) To make the process durable in solutions of alkali or acid.

The inert SAM having either a methyl or CF_2 group is formed on the SiO_2, after removing the SAM partially by ultraviolet rays etc., a reactive SAM having an amino group is then applied. When creating the SAM on SiO_2, there are two methods; solution based method and vapor deposition method. It is easy to obtain a stable SAM by using the solution-based method for the amino group, and the vapor method for CF_2. The thickness of the oxide film of SiO_2 is 20 nm, and we adopted the process to create it as a thermal oxide film stably at 800 °C. Figure 6 shows the outline of the integrated biosensing devices using two kinds of the SAM and FET.

*5: This is a characteristic that could be due to enantiomers.

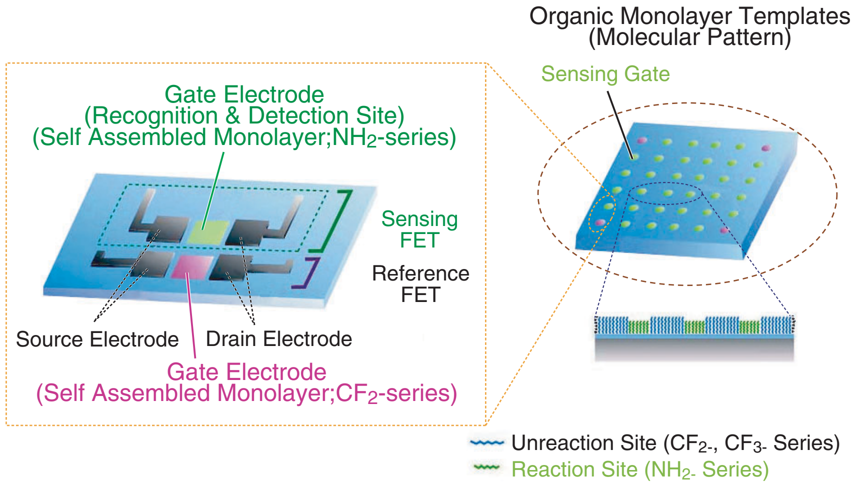


Figure 6 To Fabricate On-chip Integrated Biosensing Devices

Figure 7 shows an example of the biosensing device used as a pH sensor using this SAM technique combined with this advanced FET process. Miniaturization to 1/1000th the size or less of conventional sensors is now possible. An interesting point is that even the reference electrode is created with the same system, the total system is now becoming very fine and miniaturized.

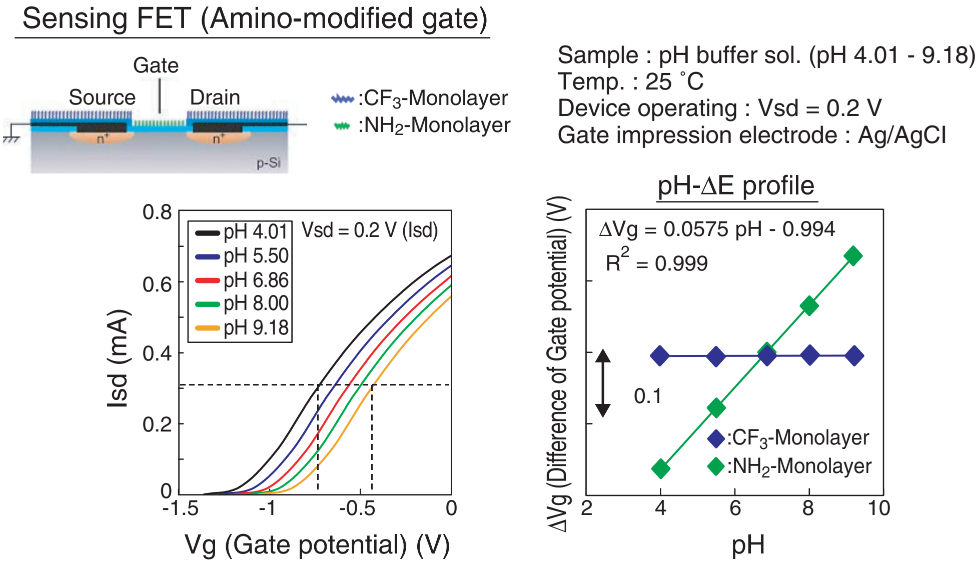


Figure 7 pH Responsibility of Amino-monolayer Modified FET

Conclusion

We have synthesized films having various functions by combining electrochemistry and nanotechnology, fabricated highly efficient materials, and have tried material fabrications that will find many uses.

In particular, we would like to develop research into controlling at the molecular and atomic levels, which is a fundamental one, while always maintaining an open mind.

<Extracted from the Screening Committee Lecture for the Dr. Masao Horiba's Award (June 22, 2004)>