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# Control and Evaluation of Surface Superstructures

Shumpei MIYAJIMA*1 Maki SEKOGUCHI*2
Tooru MATSUMIYA*1 Yuji KUBO*1
Satoru TANAKA*1

**Abstract:**

***Nippon Steel has developed a production technology for nano-space lab. substrate having surficial large periodic superstructures of oxide thin layer and graphite as well as a technology for evaluation of its surface characteristic distribution at the nano level. In oxides, optimization of sputtering conditions showed that the surface nano unevenness structure is controllable. In graphite, solid phase precipitation from palladium showed that large periodic superstructures of electron density can be formed. At the same time, Nippon Steel has developed a scanning probe microscopy (SPM) technology for evaluation.***

## 1. Introduction

In the coming 21st century, it is expected that there will be a demand for high performance materials, e.g., adaptive materials and intelligent materials, based on novel concepts unlike that of current materials. Development of such high performance materials will need material development research based on a new viewpoint, which controls and utilizes electron states, chemical bonding and material transportation in nano-meter regions. 0A concept of "nano-space lab." is that a unique space of nano-meter scale is formed in a material, and this space is considered an extremely experimental case for discovering new phenomena and producing new materials.

The Science and Technology Agency established the "Project for New Material Production using Nano-space Lab.", based on Special Coordination Funds for Promoting Science and Technology, which is to last for five years from 1994. The nano-space lab. has three-dimensional (cluster, in-crystal large defect), two-dimensional (surface structure, unevenness) and one-dimensional (quantum wire) forms. Regarding functions, the nano-space lab. can be classified into those utilizing electron-to-electron interaction, those utilizing electron-to-light interaction, and so on. The Project set seventeen research themes based on the above classification criteria and is under way with portions of the work allotted to various industrial and government research institutes.

Nippon Steel's responsibilities, among the seventeen themes, are "Surface Nano-space Large Periodic Superstructure Control and Reaction Evaluation". The purpose is to develop a technology for controlling a surface nano-space large periodic superstructure (Large Periodic Structure: LPS) as one of two-dimensional nano-space labs and a technology for evaluating surface characteristic distribution in the large periodic superstructure at the nano level. One of the aims of this research is to make a substrate which enables discrete surface immobilization to occur in a very large molecule as a useful method for analysis of biochemical reactions on the spot. Nippon Steel has developed a production technology for a nano-space lab. substrate having surficial large periodic superstructures of thin oxide films and graphite as well as a technology for evaluation of its surface characteristic distribution at the nano level. This paper reports these developments.

## 2. Preparation and Evaluation of Oxide Nano-space Lab. Substrate[1)]

It is widely known that during the process of thin film formation, film materials are often produced in island shapes in the substrate surface before the formation of a continuous layer of film. In the present research, this phenomenon was utilized as a technology for forming islands of different kinds of materials on an oxide single crystal and thereby making a surface nano "concave" structure.

A sapphire single crystal was used as a substrate, and a very thin film of titanium oxide was formed by an RF magnetron sputtering method under a mixed gas atmosphere of Ar and $O_2$ with a Ti plate as

*(1) Technical Development Bureau

*(2) Technical Development Bureau (Presently, Matsushita Giken Co., Ltd.)

a target. Film forming conditions which include pressure of atmosphere, RF output, introduced gas composition ratio, and so on, were changed over a wide range by magnetron sputtering in an effort to determine conditions favorable to the formation of a stable uneven structure. In the experiment, a film forming speed was first measured by changing parameters for (1) RF output, (2) total pressure of the atmosphere during thin film growth and (3) ratio of introduced Ar and $O_2$, then films having average thickness of 1 nm to 10 nm were formed based on the measured speed, and the respective surface structures were observed by AFM (Atomic Force Microscope).

The result of the observation showed that, depending on conditions, a nano-level titanium oxide island structure was formed on the substrate to provide an uneven surface nano structure. **Photo 1** shows a representative example. Concerning optimal conditions for making uneven stable nano structures based on relations between the respective film formation parameters and surface structures, it was found that pressure of the atmosphere should preferably be set to about 1.33 Pa, ratio of Ar and $O_2$ partial pressures to about 2:1 and RF output to about 0.5 kW. These results will be considered below.

An optimal value for pressure (total pressure) of the atmosphere was about 1.33 Pa. This is because, if the pressure is much lower than this optimal value, energy of flying-in titanium oxide particles is high and the nano structure being grown may be destroyed. Conversely, if the pressure is too high, the deposition rate is naturally increased, islands are combined together on the surface while the reaction rate for forming a nano structure cannot keep up with this and, consequently, the degree of unevenness is decreased. For a correlation between pressure of the atmosphere and nano structure, RF output power is also an influencing factor for flying-in speed of vapor-deposited particles in the case of sputtering. Although there is certain device dependency, generally, optimal nano structure can be formed under near-normal conditions where magnetron sputtering is applied.

The optimal ratio of introducing Ar and $O_2$ was about 2:1. This is because, if the proportion of oxygen is higher than this optimal ratio,

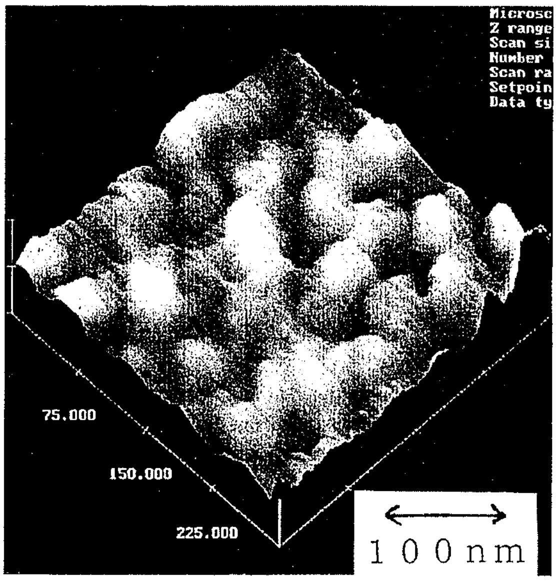


**Photo 1 Example of oxide nano-space lab. substrate preparation (conspicuous unevenness structure under optimal condition) RF: 0.5 kW, total pressure: 1.33 Pa, Ar:$O_2$ (flow rate ratio) = 2:1**

the target surface is oxidized relatively deeply, Ti reaches the substrate surface in an already oxidized state and, consequently, its movement is more difficult compared with the case where it is dispersed on the surface while being subjected to oxidation reaction. Therefore, growth of an unnecessarily sharp projection occurs. Conversely, if the proportion of oxygen is very small, the formed thin film is incompletely oxidized and thus it is not practical in terms of stability. If the ratio of Ar and $O_2$ is set to about 2:1, the above problems are avoided, and an optimal nano structure can be formed.

## 3. Establishment of Surface Characteristics Distribution Evaluation Technology by AFM[2)]

For discretely immobilizing a very large biological molecule of protein or the like on the surface nano-space lab. substrate, evaluation of surface characteristic distribution in aqueous solution is important. Therefore, investigation was made for a technology for evaluating nano-level surface unevenness and electric charge density distribution in aqueous solution with good sensitivity by using a tapping mode AFM. Nano Scope III and Multi-mode SPM units available from Digital Instruments Company were used.

First, it was confirmed that titanium oxide/sapphire surface unevenness can be observed highly accurately in KOH aqueous solution. Then, evaluation of a surface electric charge density distribution by AFM was tried. For the titanium oxide/sapphire surface in aqueous solution, an OH group probably appears on the uppermost surface because of interaction with water. Since points of zero charge (pzc) in aqueous solution are different for a titanium oxide and sapphire, there is a possibility that, by adjusting the pH of the solution to a proper value the electric charges in the OH group can be distributed between positive and negative sides at the nano scale. It has been reported that pzc of titanium oxide is about 6.7 and that of sapphire is about 9.1. Thus, a sample was dipped in KOH aqueous solution of pH = 8.04, which is nearly midway between the above pH values, and measurements were performed. For detection of electric charges of a very small surface area, the Force Calibration Plot function of the multi-mode SPM was used. In this Plot, attracting forces are observed immediately before a probe touches the surface (for approaching) and also immediately before the probe leaves the surface (for retracting). Thus, by measuring these forces, the surface electric charges were estimated.

As a result of comparing the Plots for several kinds of samples differing from one another in titanium oxide film thickness, it was verified that average attracting forces in all the scanning ranges are larger in the order of sapphire (no thin films) > titanium oxide average film thickness 1 nm > titanium oxide average film thickness 3 nm and thus titanium oxide shows a smaller attracting force than sapphire. In addition, it was confirmed that surface electric charges represented by attracting forces are distributed at the nano scale, though qualitatively.

## 4. Preparation of Carbon/Palladium Nano-space Lab. Substrate[3)]

It has been reported in recent years that a clean graphite surface shows LPS which is several tens of times larger than the distance between atoms closest to each other. This LPS is easily prepared by adding very small disturbances to the surface, for instance by depositing a small amount of metal such as silver in an island form on highly oriented pyrolytic graphite (HOPG). This LPS is observed in the vicinity of a step sometimes even in the case of non-treated HOPG. The substance of LPS has been described as a kind of Moire pattern, where a graphite surface first layer atomic plane takes the structure of being rotated against the bulk arrangement of a second layer and lower, but the detail of its production mechanism remains to be clarified.

In the present research, in an effort to find a method of forming a new type LPS as a nano-space lab. substrate, precipitation of carbon solution-treated in metal Pd was investigated. In the latter half of the graphitizing process of industrial graphite production, a transition metal such as Fe, Co, Ni or Pd can be used as a catalyst for advancing reaction at low temperature. In the present research, by obtaining a hint from the above, basic investigation was made into a technology for forming a surface having LPS by precipitating carbon solution-treated in a Pd single crystal in ultra-high vacuum and forming a graphite layer on the Pd surface.

For the Pd single crystal, two kinds of disks having a diameter of 6 mm and thickness of 2 mm (Metal Crystals & Oxides Ltd., England) and having surfaces (111) and (100) were used. Graphite precipitation on Pd was carried out in two stages. The first stage was solution treatment of carbon on Pd, and the second was precipitation of solution-treated carbon on the Pd surface. First, the surface of the Pd single crystal was covered with carbon (Tokai Carbon, 99.99%) by vacuum evaporation. Then the treated Pd single crystal was introduced into a silica tube and held at 1173 K for two weeks. Graphite powder was added at the time the single crystal was introduced into the silica tube. This assures that there is an excess of carbon. After heat treatment, the single crystal was put into water for rapid cooling and, after a surface having specified surface orientation was ground by a machine, the Pd single crystal was subjected to ultrasonic cleaning in acetone. Then, the carbon-super-saturated Pd thus produced was heated to a specified temperature in an ultra-high vacuum chamber and graphite was precipitated. Pressure of the atmosphere was kept at $1 \times 10^{-6}$ Pa or lower during the precipitation, and by using those heated at 923 K, 998 K and 1073 K as samples, surface unevenness and surface electron densities were observed by STM.

An ultra-high vacuum STM system was structured so that a UHV-STM 1 available from Omicron Company was connected to an ultra-high vacuum chamber using an ion pump. A Nano Scope III controller available from Digital Instruments Company was used as its control system via an interface.

The result of STM observation showed that in the case of the sample having surface (100) and heated at 923 K, there were no orderly atomic images special to normal graphite, distorted triangular grids were seen only on the limited parts of the surface and thus in sufficient graphitization progressed. In the cases of the samples having surface (100) and heated at 998 K and 1073 K and the sample having surface (111) and heated at 1073 K, most of the parts of the respective surfaces were graphitized. For these high temperature treated samples, various regions of the sample surfaces were STM-observed to find places where LPS structures appeared. As a result, it was confirmed that LPS easily appears in the vicinity of a step on the surface and there are various LPS periods from 3 nm to 7 nm. **Photo 2** shows an example of LPS prepared in the present research where both atomic images and LPS are clearly observed.

Concerning image brightness and darkness corresponding to apparent unevenness in STM images, two contributing factors are generally known, i.e., real geometrical unevenness (atom displacement) and surface electron density difference. Since it was not clear which factor contributes more to the graphite LPS structures, AFM observation was applied for places where LPS structures were observed by STM. Although graphite detected atomic images were clear (see **Photo 3**), no large periodic orders equivalent to LPS were found at all.

In STM measuring in Constant Height Mode, scanning was carried out while distances between the probe and the samples were kept constant for recording changes in tunnel current values and, in this case, clear LPS images were obtained. Accordingly, contribution by the surface electron difference was discovered to be predominant. Further, for comparing differences in electron structures between the bright and dark parts of LPS images, I–V curves in both regions were measured (see **Fig. 1**). Tunnel current values differed greatly between the bright and dark parts when a bias voltage of ±0.4 V was applied. Also, clear differences appeared in the shapes of curves. Thus, the existence of differences in electron structures for both the aspects was verified.

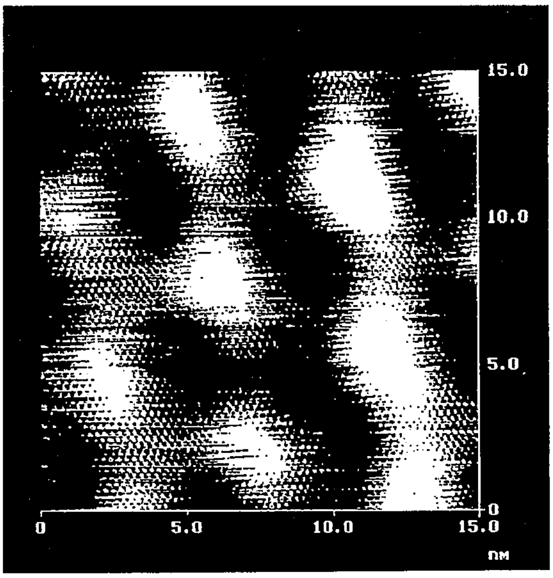


**Photo 2 Graphite LPS structure precipitated from palladium (both atomic image and large periodic structure are seen)**

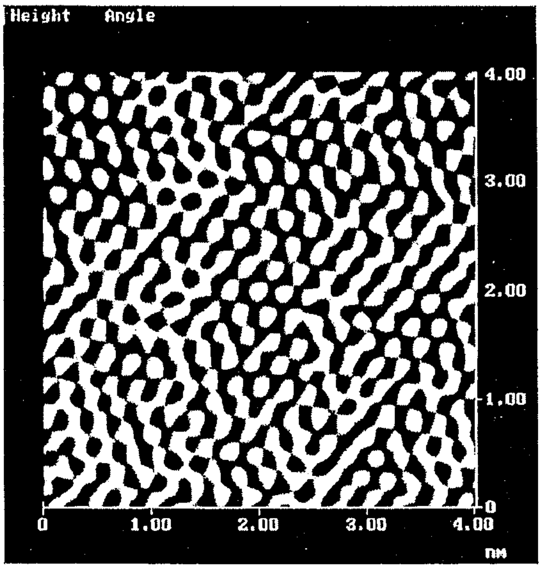


**Photo 3 AFM image in region where LPS structure is observed by STM (atomic image is clear but LPS structures are not seen)**

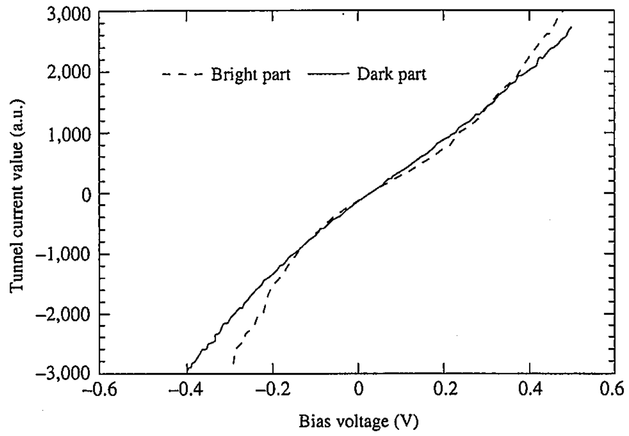


**Fig. 1 I–V curves for bright and dark parts of LPS structure**

Because of its very orderly periodicity, it has been understood that graphite LPS is produced because of the abnormality of a first layer in a layer structure. In other words, graphite LPS can be understood as a kind of Moire pattern which occurs because a two-dimensional structure symmetrical by six times has an arrangement where only the first layer of the surface is rotated by several times against the second layer or lower. Clarification of what type of LPS appears depending on orientation of the Pd surface and treatment temperatures is a very interesting task for a deeper understanding of LPS phenomena. However, its details remain to be clarified.

## 5. Nano-space Substrate Preparation by Oxide Substrate Chemical Modification

AFM observation of biological molecules faces the technology problem of making samples for immobilizing molecules in as wide a state as possible so as to observe the details and the technology problem of observing without disturbing the states. In the present research, observation was tried of protein adsorbed on inorganic oxide thin film surfaces in order to develop a technology for observing biological molecules by AFM.

For oxide substrates, a sapphire single crystal and sapphire deposited by sputtering oxide thin films ($TiO_2$, $TiSiO_x$ and $ZrO_2$) on these surface were used. For protein, bovine serum albumin (BSA) was used, and AFM observation was tried in phosphoric acid buffer solution (pH7.2).

For an AFM observation technology, proper substrate selection and adjustment of probe force for immobilizing molecules during scanning are important. First, a substrate made by directly adsorbing protein on a sapphire surface was observed. But no molecules were found. When a substrate made by depositing an oxide thin film was used, molecule was found by adjusting the pressing force of the probe. Comparison and observation were made on BSA adsorbed on $TiO_2$, $TiSiO_x$ and $ZrO_2$ under an optimal pressing force. Among these, for the $TiSiO_x$ substrate, molecules were observed while the pressing force of an AFM cantilever was large, and BSA adsorption in a well developed state was seen. Differences in BSA adsorption by oxide thin films used for substrates may be attributed to size relations between thin film components and BSA points of zero charges. However, the details are not yet clear.

## 6. Conclusion

Nippon Steel has developed a technology for production of nano-space lab. substrates having surficial large periodic superstructures of oxide thin layers and graphite and a technology for evaluation of surface characteristics distribution thereof at the nano level. In the case of oxides, an island shape growth occurs in the initial process of thin film formation by sputtering, and this phenomenon was used for forming a nano-space lab. substrate. Then, it was found that optimization of conditions enables the structure of surface unevenness to be controlled. In the case of graphite, it was found that solid phase precipitation from palladium enables a large periodic structure to be formed. In this structure, the change in electron density is predominants rather than atom displacement. At the same time, high level AFM and STM technologies for evaluation were developed.

The present research is only basic and is not directly related to any particular material development. But Nippon Steel intends to utilize the results of this research for various applications. These applications, in addition to discrete surface immobilization of very large molecules useful for on-the-spot analysis of biochemical reaction as described in the Introduction, also include texture of metallic material surfaces, product appearance, unevenness control for a material as a carrier substrate such as a catalyst, and others.

The present research was carried out as a part of the Science and Technology Agency's "Research for New Material Production using Nano-space Lab." based on Special Coordination Funds for Promoting Science and Technology from 1994 to 1997.

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