NIMS NOW

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Discovery of New Ternary Gate Oxide Material Using Combinatorial Synthesis and High-throughput Characterization

Parhat Ahmet, Toyohiro Chikyow
Nanomaterial Assembly Group Nanomaterials Laboratory

The development of electronic devices is now approaching a historic turning point. Up to the present, Si, Al, and SiO_2 have been used as the basic materials for silicon devices. However, with progressively higher integration and miniaturization, new materials are required as replacements for those used thus far. The most important task will be the development of a new gate insulation film technology. Although SiO_2 has been used as a gate material to date, problems arise when the film thickness is reduced to less than1.5nm, because tunnel current increases due to the thinness of the material, and as a result, the leak current value increases. Discovery of a material with a higher dielectric constant (permittivity) than that of SiO_2 would eliminate the need to reduce the thickness of the gate insulation film, and thus would avoid increased leak curent. For this reason, a material with a higher dielectric constant than SiO_2, or socalled High-K material, is desired.

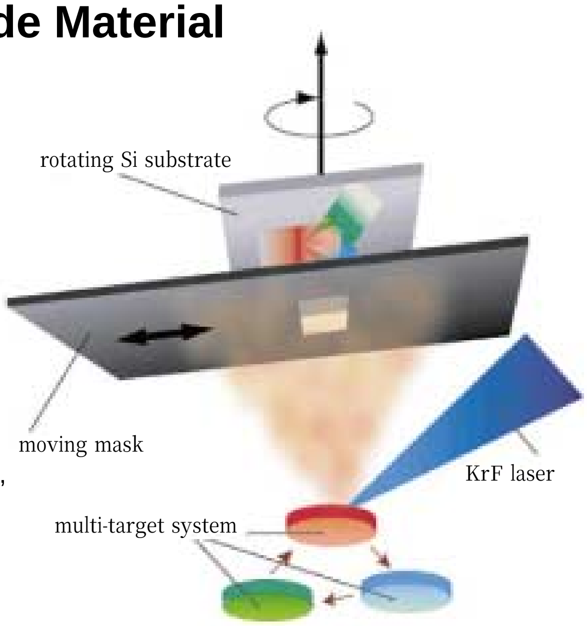

Fig.1: Conceptual diagram of multi-element combinatorial thin-film material deposition method. Ternarycombinatorial synthesis is possible using substraterotation and moving masks.

The following four conditions will be required in next-generation gate oxidation films:
1) Thermally stable amorphous structure
2) High dielectric constant (relative dielectric constant $\varepsilon \geqq 15$)
3) Clean interface formation with Si
4) Durability under reduced atmosphere pressure in hydrogen.

However, it is difficult to develop new oxide materials which satisfy these conditions simultaneously and urgently. To give an answer to this problem, the Nanomaterial Assembly Group developed a " multi-element combinatorial thin-film synthesis system, " which is capable of producing a film with a composition spread on a substrate while continuously controlling the compo-sition of three materials.

Figure 1 shows a schematic illustration of the combinatorial material synthesis process, in which the multi-element composition spread method is applied with moving mask system and substrate rotation. Pulsed Laser Deposition (PLD) is used as the film deposition method. As shown in the figure, a film with a continuously controlled composition consisting of three elements can be deposited in a one-atom layer by splitting laser irradiation among three targets.

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RESEARCH FRONTLINE

>In this issue

NIMS NEWS

Prof. Horiike Joined as the First NIMS Fellow

NIMS has newly established a system where researchers who have reached prominent achievements in the field of materials science and are expected to make large contributions to NIMS are invited as NIMS Fellows.
Prof. Yasuhiro Horiike of Graduate School of Engineering, the University of Tokyo assumed the position of the first NIMS Fellow.

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Discovery of New Ternary Gate Oxide Material

Using Combinatorial Synthesis and High-throughput Characterization

Parhat Ahmet, Toyohiro Chikyow
Nanomaterial Assembly Group Nanomaterials Laboratory

By repeating this operation, it is possible to prepare ternary alloying at a certain temperature in an experiment. This method also has the advantage of enabling simultaneous formation of a binary region in the vicinity of the ternary region. All operations necessary for deposition of the thin film, including substrate rotation, target conversion, and mask motion, are computer-controlled.

Currently HfO_2 and ZrO_2 have been focused as gate oxide materials. However, from the viewpoint of the empirical glass rule, these materials are intermediate oxides, which mean that an amorphous structure cannot be obtained by themselves. To make them amorphous materials, it is necessary to mix network forming oxides and modified oxides. We selected Al_2O_3 and SiO_2 as network forming oxides and Y_2O_3 and $Al2O_3$ as modified oxides and prepared phase diagrams for several combinations of these oxides. The dielectric constant was measured with a microwave microscope, which is capable of evaluating permittivity without forming an electrode to the specimen. For structural characterization, a combinatorial X-ray diffraction system (see attached) was used for identifying phases and transmission electron microscopy (TEM) was used for the local observation. Here the TEM samples were prepared by the micro-sampling method, which allows preparation of electron microscope specimens from designated areas.

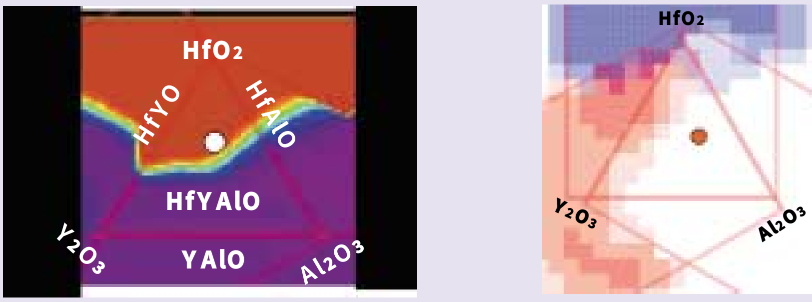

Fig.2 (left): Distribution of dielectric constants measured by microwave microscope. Red indicates regions with a high dielectric constant. (right): Crystallographic characterization by combinatorial X-ray diffraction. The region shown in color has crystallized; that shown in white is amorphous.

The results of a series of material characterizations showed that a high dielectric constant can be obtained over a comparatively wide area with an HfO_2–$Y2O_3$–$Al2O_3$ composition. The results of combinatorial X-ray observation indicated that an amorphous region exists within this area. Figure 2 shows the condition of the amorphous region.

Figure 3 is a cross-sectional image taken from the HfO_2 : Y_2O_3 : $Al2O_3$ = 6 : 1 : 3 area in this region. Although a silicate layer approximately 0.4nm in thickness formed at the interface with the Si substrate, the ternary compound region itself maintains its amorphous nature. This structure remained amorphous after post-heat treatment at 700 degrees, demonstrating that the film is thermally stable. This result is extremely significant, as it led to the discovery of a new gate oxide film which was previously unknown.

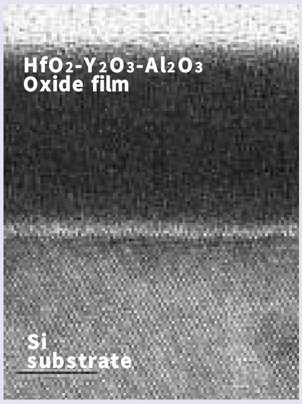

Fig.3: Structural characterization by TEM. An amorphous structure was confirmed in the area indicated the red circle in Fig.2.

Future issues in device development will include the search for new materials which give improved functional performance and accelerated development of nano-level process technologies. Speed and innovation will be essential requirements for 21st century electron device development, and, as demonstrated by the present research, the combinatorial method is the unique technique which meets these needs. In the future, combinatorial techniques will be applied not only to gate oxides, but also to the development of other functional materials on silicon.

Note: We wish to thank Dr. Mamoru Watanabe and Dr. Kenjiro Fujimoto of the Advanced Material Laboratory in NIMS for their generous assistance in performing X-ray diffraction characterization.

Annual Plan and Budget for Fiscal 2003 (Research Budgeting Office)

In March this year, the " annual plan for fiscal 2003 " was submitted to the Ministry of Education, Culture, Sports, Science and Technology. Since (MEXT) fiscal 2003 is the third year of the Mid-term Plan, this annual plan defines the activities to be carried out in fiscal 2003 based on the progress made to date for achieving the targets established by the Mid-term Plan. For further details, see http://www.nims.go.jp/nims/former/mission/nedo15.pdf

The budget for administrative expenses which exceeds previous year was approved despite the severe financial condition of the government. The facility expenses include the funds to construct the nano-biomaterials laboratory building and the 1-GHz-class high-resolution NMR facility in this year. The consigned research revenue was significantly increased from the previous year since the R&D projects for "Economic Vitalization" sponsored by MEXT start this year.

Copper and Boron Nitride Composite Coating for Stabilization of Vacuum Pressure

Tetsuo Oishi, Masahiro Tosa, Micro-nano Component Materials Group,
Materials Engineering Laboratory
Yoko Konishi, Department of Chemical Engineering, University of Illinois at Urbana-Champaign

The inner wall of a vacuum chamber in a vacuum chamber cylinder was coated with a composite of copper and boron nitride by a newly developed rotating evaporation electrode. Pressure increase in the chamber was suppressed and ultra-high vacuum (less than 10-5 Pa) was successfully stabilized over a long period of time.

Vacuum pressure in a chamber depends on the extent to which a gas released into the inner space of the chamber is evacuated to the outside atmosphere by the vacuum pumping system. Major factors affecting the increase of the pressure in a vacuum chamber are gas molecules adsorbed on the inner wall surface and hydrogen released into the inner space by diffusion permeation through the wall.

The amount of gas adsorption is proportional to the surface area. The conventional method for reducing the amount of gas adsorption is, therefore, to reduce the surface area of the inner wall by making it ultra-smooth by means of mirror polishing. However, there is a limit in reducing the surface area by smoothing. Furthermore, this method has a problem in the fact that it does not have much effect for suppressing the hydrogen permeation.

Hexagonal boron nitride (BN) is a ceramic that scarcely adsorbs any gas. We have already developed a technology for coating the surface by this BN at a low temperature. It was found that the BN coating film has a property of suppressing the hydrogen permeation. Generally, the BN film is brittle and poor in adhesiveness with the stainless steel chamber material. We have developed a new technology for making it a lubricating, strong coating film by co-sputtering it with copper. Since hydrogen has a low solubility in copper, this film is expected to have an effect of suppressing the diffusion permeation of hydrogen. In order to coat this Cu-BN film on the inner wall of a vacuum chamber, we experimentally fabricated a system where a sputter vapor deposition electrode moves back and forth while rotating.

The experimental co-sputter deposition system is schematically illustrated in Fig. 1. Using the target material attached to the electrode, this system can coat the inner wall of a vacuum chamber that is 15 cm in inner diameter and 40 cm in inner cylinder length. It took approximately 20 hours to uniformly coat the whole inner wall surface of the chamber as shown in the photo below.

Photo: A vacuum chamber without any coating onto an inside wall (left: silver wall) and the vacuum chamber with coating of mixture of copper and boron nitride onto the inside wall (right: copperish magenta wall).

The vacuum pressure stability in the chamber with the Cu-BN coated inner wall was invest- tigated. The result is shown in Fig. 2. The pressure gradually increases after the chamber was sealed off from the vacuum pumping system when the pressure reached a designated vacuum level. It is clear that the chamber with the Cu-BN coated inner wall shows significantly smaller pressure increase than the one with the no coated inner wall.

This method that can stabilize the ultra-high vacuum is expected to make substantial contributions to life prolon- gation, energy conservation, downsizing, realization of extremely high vacuum (less than 10^{-10} Pa) in the vacuum industries such as surface analyzers and high-voltage vacuum circuit breakers.

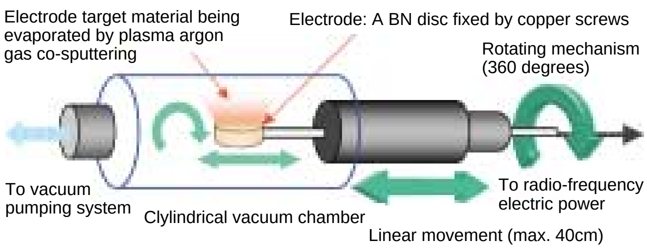

Fig. 1 Schematic drawing of the newly developed Cu-BN coating system, coating the chamber inner wall with co-sputter deposition

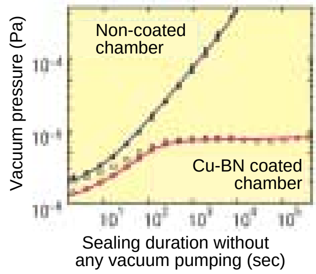

Fig. 2 Vacuum pressure increase in vacuum chambers

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Editor:
Masatoshi Nihei
Phone: +81-29-859-2026
E-mail: NIHEI.Masatoshi@nims.go.jp

Masahiro Tada
Phone: +81-20-859-2026
E-mail: TADA.Masahiro@nims.go.jp

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Assuming the position of NIMS Fellow

I retired from the University of Tokyo at the end of March this year, and joined NIMS as of April 1. I intend to make every effort for achieving research results worth the position of a NIMS Fellow. The first target is to develop a health-care chip and systematize it in corporation with the industry, academia, and public sectors, aiming at realizing a system where a minute amount of blood collected by a no-pain needle is analyzed and multiple health and disease markers are diagnosed at home. I will also challenge the tasks of developing an implant chip by fusing the bio and nano technologies as well as a diagnosis and treatment method based on single-molecule recognition. Toward these ends, I hope to be provided with supports from related persons and organizations.

Yasuhiro Horiike

Doctor of Engineering. Graduated from the Dept. of Applied Physics, Graduate School of Engineering, Waseda University in March 1968. Tokyo Shibaura Electric Co., Ltd. (current Toshiba Corporation). Professor to the Faculty of Engineering at the University of Hiroshima. Professor of the Graduate School of Engineering, the University of Tokyo. Joined NIMS as of April 1, 2003.

Direct Observation of Local Thermal Vibration Anomalies in Quasicrystalline Solids

Eiji Abe
Aperiodic Solids Research Group, National Institute for Materials Science

Quasicrystals are unusual solids that do not exhibit the periodicity of ordinary crystals, but do possess a kind of long-range order that is referred to as quasiperiodicity. Theory predicts a localized thermal fluctuation phenomenon called a phason, which is peculiar to quasicrystals, but no experimental data has been obtained on the actual spatial distribution of this phenomenon, that is to say 'where' in the quasicrystalline solid it is conspicuous.

We have used a scanning tunneling electron microscope combined with an annular dark-field detector (ADF-STEM; see Fig. 1) to obtain atomic-level images of an aluminum-nickel-cobalt compound quasicrystalline solid (bottom right) at room temperature (approx. 20℃) and at high temperature (approx. 830℃). Because the annular detector mainly captures thermal diffuse scattered electrons, the image intensity is sensitive to the amplitude of the thermal vibration of the atoms. The observations reveal that the image intensity at particular positions increases remarkably at high temperature (Fig. 2). This increase in intensity can be well explained by a (relatively) abnormally large amplitude of thermal vibration of the aluminum atoms that are in those positions. The thermal vibration anomalies at these specific aluminum atoms can be interpreted as phason fluctuations, making this the first example of direct capture of phason fluctuation in a quasicrystal at the atomic level.

These results represent the first direct observation of local thermal vibration anomalies in a bulk solid, regardless of periodicity or non-periodicity. We have thus demonstrated that the electron microscope is capable of obtaining information on not only the atomic configuration of solids, but also extremely minute displacements of atoms such as being due to thermal vibrations (on the order of 0.01 nm). This is significant, because the local thermal vibration anomalies and minute distortions are factors that directly govern the physical characteristics of the substance. We have high expectations for the future development of the method demonstrated in this research as a new method of nanoscale physical measurement of substances and materials.

This research, in part, was conducted as a part of the strategic creative research program of the Japan Science and Technology Corporation under the theme " Creation of new materials by using quasiperiodic structures (Research representative: Sai An-po) ". (The results of this research have been presented in various media, including the Nikkan Kogyo Shimbun, the Japan Industrial Journal, the Sankei Shimbun, the Chemical Daily and Science News.)

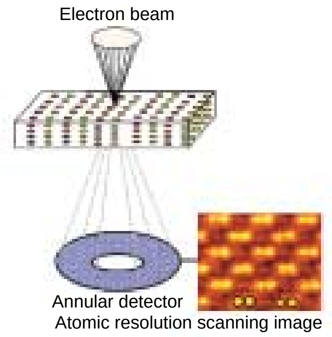


Fig Figure 1: Atomic image formation in ADF- STEM.ure An extremely fine electron beam is scanned two-dimensionally over the sample and the intensity of electrons scattered at certain angles by the atoms is measured by an annular detector.

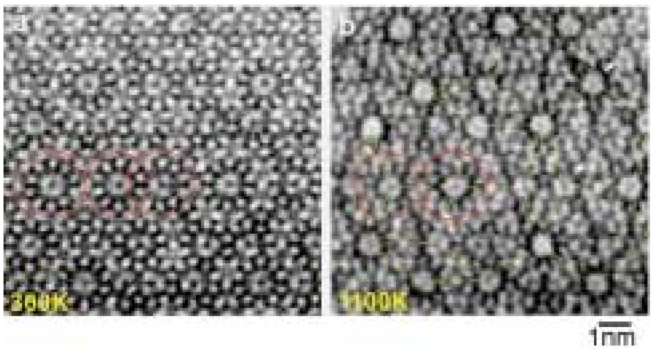
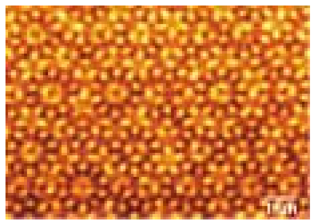


Figure 2: Atomic image of Al-Ni-Co decagonal quasicrystal obtained by ADF-STEM. The image shown in (a) was obtained at room temperature (approx. 20℃) and (b) was obtained at high temperature (approx. 830℃). The decagon shown in red in the figures is a cluster of atoms that is considered to be the structural unit of this quasicrystal. At high temperature, the contrast becomes remarkably high in the vicinity of the centers of special clusters that are on the quasilattice points represented by the pentagons (yellow dotted lines in b).



Atomic-resolution ADF-STEM image of an Al-Ni-Co quasi-crystal

PRESS RELEASE

Discovery of Metallic Electrical Properties of Electron

Tomonobu Nakayama, Electro-nanocharacterization Group, Nanomaterials Laboratory
Jun Onoe, Associate Professor, Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology

Fullerene molecule C_{60} is a stable nano-cluster of approximately 0.7 nm in diameter that is composed of 60 carbon atoms. In recent years, carbon nanotubes (CNT), which are also composed of carbon atoms, are attracting extensive interests due to their excellent properties. However, C_{60} is still an attractive carbon- based nanomaterial due to the following two points.

Firstly, its refining and mass-producing technologies are well established, whereas CNT has many problems yet to be solved. Secondly, the C_{60} molecule has a mass much smaller than CNT, which allows it to be treated just like an atom, making it possible to apply conventional technologies such as ultra-high vacuum molecular beam epitaxy.

With regard to the C_{60} nanofilm that has an extremely small thickness equivalent to one to one hundred molecules and the C_{60} nanowire with an extremely small width of the same size range, electrical properties should be controlled and evaluated in view of using C_{60} molecules in nanoscale electronic devices in the future. However, it is difficult to add impurities uniformly in nanoscale structures, and their electrical properties have not been measured successfully to date.

We are investigating how to control the electrical properties of nanostructures composed of C_{60} without adding impurities. By using Fourier transformation infrared spectroscopy, we analyzed the intermolecular bond in the C_{60} nanofilms that were irradiated by electron beam (EB) in ultra-high vacuum. We confirmed that a unique bond is induced between C_{60} molecules (Fig. 1), resulting in the polymerization of the C_{60} nanofilms.

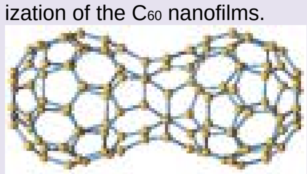


Fig. 1 Schematic drawing of intermolecular bond induced by electron beam irradiation
(polymerization of two molecules)

Award given to NIMS president

The Japan Institute of Metals recently gave Teruo Kishi, NIMS President, the Academic Contribution Award. This award is to his great contribution to the metal industry and research on metals and promoting various research projects at NIMS for decades.

"Non-destructive Evaluation of Materials and Smart Materials" was delivered at the 48th Honda Memorial Lecture Meeting held as part of the 2003 Spring Conference of the Japan Institute of Metals. The meeting has similar function as other international memorial lecture meetings held overseas. The main purpose of this meeting is to make participants interested in materials research by discussing the progress in fundamental and application technologies in various fields. Honda Memorial Lecture Meeting is one of the most prestigious academic meetings in Japan.

Memorandum with University of Washington for research cooperation

On March 18, 2003, NIMS' Nanomaterials Laboratory signed a memorandum with the Faculty of Engineering, University of Washington to promote the research collaboration in the field of nanomaterials.

This collaboration aims at developing a technology to identify an optimum

material composition and synthesis condition quickly which allows making a new material for practical use in a short period of time. For achieving this aim, the combinational method will be employed, which speeds up the steps from synthesis of multiple-element materials of various compositions to their evaluation and allows identifying a target material quickly.

NIMS' Nanomaterials Laboratory has already started research activities in the nano-bio technology, a new field that combines the nano-structure forming technology with the biological technology. On the other hand, the University of Washington is highly reputed in bio-chemical research in the medical field. The combination of the potential and expertise of the two organizations is expected to open the way to the new nano-bio field.

Promotion of 3-party joint research by NIMS, UT, and AIST

Based on the comprehensive agreement for joint research concluded by NIMS, the University of Tsukuba (UT), and the National Institute of Advanced Industrial Science and Technology (AIST) in March last year, the three parties reached another agreement covering issues such as the treatment of intellectual properties and confidentiality relative to the joint research to be carried out in the future.

Beam Polymerized C_{60} Nanofilm

Their electrical resistivity were directly measured at room temperature in air using four metallic probes of the multiple-probe scanning tunneling microscope (insertion in Fig. 2). The resistivility was found to be in the range of 1 to 10 ohm·cm, which is 8 to 14 orders of magnitude smaller than the values known for pristine C_{60} solid. This property was maintained under room temperature and atmospheric pressure.

The junction between the EB polymerized C_{60} nanofilm and the metallic electrode showed the ohmic property (Fig. 2). The electronic density of

states at the Fermi level was measured by using tunneling spectroscopy. The characteristics thus identified indicate that the EB polymerized C_{60} nanofilm has metallic electrical properties. At present, however, its resistivility is still far larger than that of metal. The future task is to reduce the resistivility.

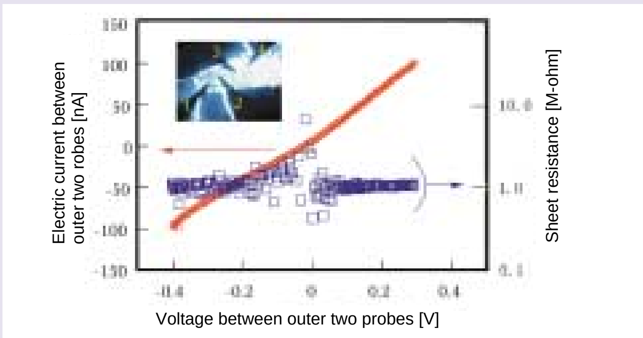


Fig. 2 Example of direct measurement of resistibity of EB polymerized C_{60} nanofilm (thickness: 70 nm).
The red data shows the ohmic property with electric current proportional to applied voltage. The blue data shows the resistibility of the film. The insertion is a scene of the measurement.

It is expected that these results open the way for using the C_{60} molecules in nanoscale electronic devices as well as for developing ecological devices that utilize carbon resource that exists abundantly on the Earth.

(These research results have been reported in related newspapers, including the Nikkan Kogyo Shinbun, Japan Industrial Journal, Chemical Daily, and Science News, in the Japanese language.)

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