Final Reports of Groups

Information Storage Group

Katsuji Nakagawa*, Akiyoshi Itoh, Arata Tsukamoto

1. Research Purpose

The information storage group pursues fundamental research to quest for high-density and high-speed memory for going green technology.

2. Advances and achievements in 2009

A high-speed recording and huge capacity for storage are extremely precious to our society. The phenomenon of a photo-induced magnetization applying a femto-second laser, which was revealed by our members, suggested a possibility to dramatically improve the high-speed recording of information technology. Besides, utilizing nano-technology fabrication for a near-field antenna and recording materials, huge capacity will be achieved. $Gd_x(Fe_{87.5}Co_{12.5})_{100-x}$ as a rare-earth transition metal alloy film was studied. Optical Parametoric Amplifier (OPA), which is supported by the project, was installed to probe the phenomena from 0.5 to 5 eV in energy. Substrates with nano-structured surface were fabricated to improve a high density recording prospects in active collaboration with Supramolecules and Self-Assembly Group. We also analyzed the thermal inter-diffusion of patterned recording media with thermally assisted. The particle structure of the recording media is effective to enhance memory density for the thermally assisted recording. We begun to study analyzing the filed which was close to electrode when a circular polarized light was exposed for the purpose to effectively utilize the optical induced magnetization as high-speed recording in a local region.

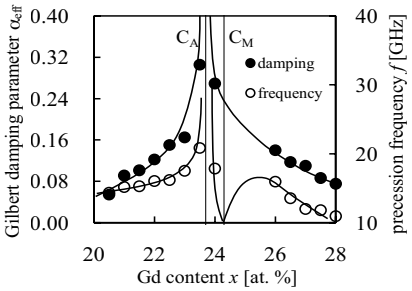


Fig. 1 Compositional dependence of damping parameter α and precession frequency f

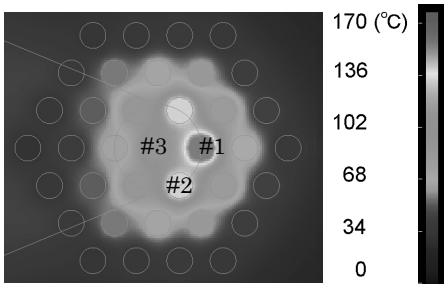


Fig. 2 Temperature increase of metallic particles heated surface plasmon antenna.

3. Advances and achievements in 2010

1) Femto-second laser and the optics have been designed and constructed to analyze the surface plasmon response.

2) Electro-magnetic transit analysis method for nano-scale dispersion materials has been developed by the cooperation with Associated Professor Ohnuki.

3) We have studied some surface plasmon antennas to find an antenna, which can create circularly polarized resonance mode. It was revealed that some antennas had a resonance mode for circularly polarized light.

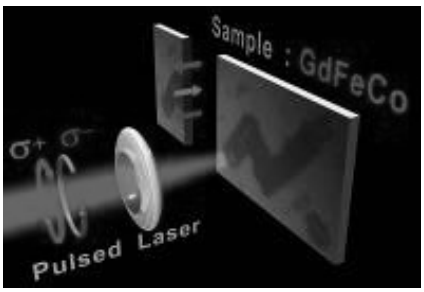


Fig. 3 The demonstration of all-optical information recording on magnetic media.

4) All-optical time resolved measurement system was constructed with femto-second pulse laser. Magnetic and optical response from material was monitored by the magneto optical effect and the change of reflectivity caused by heating of electrons, respectively. Ultrafast demagnetization phenomena were observed which must be caused by heating of electron system.

5) Perpendicular magnetized TbFeCo thin film consisted from rare earth and transition metal alloy was

prepared. We clarified that the magnetization direction of TbFeCo can be switched by irradiation of circularly polarized ultra short pulsed laser without magnetic field.

6) We have succeeded preliminarily to prepare thin SiO_2 layer on metallic films which have two dimensional closed packed nano-pores prepared by the polymer micelles technique. As another type of nano structured template having a conjugate relation with nano-pore structure, nano convex pattern was prepared by using self-assembled spherical silica particles followed by inductively coupled plasma reactive ion etching.

7) We prepared test batches of Si and metallic film by Ar ion etching and confirmed the etching rates satisfied our study.

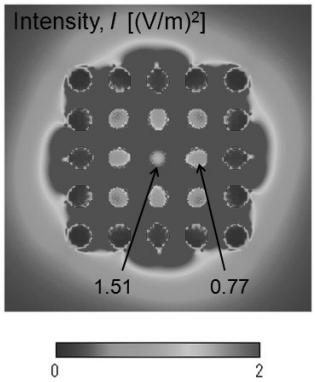


Fig. 4 A simulation result as a generated circularly polarized light into a center particle.

Collaborations and activities in 2010 as the group

We had one or two meetings every month with Associated Professor Ohnuki to find a method to calculate a surface plasmon response. The results were reported at IEEE International Symposium on Antennas and Propagation, July 11-17, 2010, Toronto, Ontario, Canada. We also invented a new antenna structure to confine a circularly polarized light, and submitted a patent. We also reported this result at 55th Annual Conference on Magnetism & Magnetic Materials, 14-18 November 2010, Atlanta, Georgia, USA.

4. Advances and achievements in 2011

1) We had trials to write magnetic domains on a magnetic film by femto-second laser. The magnetic film was coated with surface plasmon antennas which were made by E-beam lithography. The shapes of the antennas were designed by electro-magneto simulation as well as thermal diffusion simulation. From the observation of film structure dependency on optical/magnetic response during tens of ps after laser irradiation, it was found that conductive metallic layer play an important role in ultrafast energy transfer process.

We also set up the system applying a fine adjustment manipulator. Laser pumping and probing system can be easily adjusted by the new system.

2) We found some specific aperture shape which can confine a circularly polarized light. We also studied another structure for antennas which can create a localized circularly polarized light with a liner polarized light.

3) A new magnetic bias coil was prepared for applying up to 1 kOe. The bias field can be synchronized to the laser system.

4) We started to fabricate nano-meter structure using etching method. Nano-size silica particles were placed over a metal film before etching.

5) We found that the magnetization in a small one magnetic particle can be reversed by applying surface plasmon antenna by simulation.

Collaborations and activities in 2011 as the group

We have had regular meetings once or twice a month meetings every month with Associated Professor Ohnuki, belonged to Quantum Theory & Computation Group, to find a method to calculate a surface plasmon response. The results were reported at IEEE International Symposium on Antennas and Propagation, July 5-6, 2011, Spokane, Washington, USA. We had two invited talks about magnetic nano-particle media and dynamics of ultra fast magnetic reversal at Moscow International Symposium on Magnetism, Aug. 21-25, 2011, Moscow, Russia. We also reported about thermally assisted recording, ultra-high speed magnetization, and circular polarized light generation with a

plasmon antenna at Magnetic and Optical Research International Symposium, June 21-24, 2011, Nijmegen, The Netherlands.

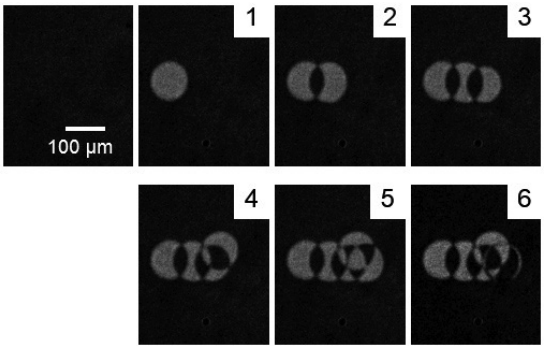


Fig. 5 Magneto-optical image of magnetic domains after single pulse laser irradiations.

5. Advances and achievements in 2012

1) Thermally assisted magnetic recording with surface plasmon antenna has been succeeded by applying femto-second laser. Three issues are key points of this success: (1) a computational analysis of electro-magnetic field as well as thermal diffusion in magnetic film, (2) a structure design of surface plasmon antenna and antenna fabrication by electron beam lithography, and (3) magnetic recording test applying femto-second laser with surface plasmon antenna. The magnetic mark of 166 nm x 120 nm was written by this method. The written mark size has not reached the size of project goal: 77 nm x 77 nm. Our progress, however, is very big, and we still go forward to our goal in the final year.

2) We found experimentally a novel magnetization reversal phenomenon in a ferri-magnetic GdFeCo film driven by an ultrafast heating of the medium resulting from the absorption of a sub-picosecond laser pulse without the presence of a magnetic field. Also relevantly to technological applications, we have shown experimentally that switching can occur when the sample is at room temperature before laser excitation.

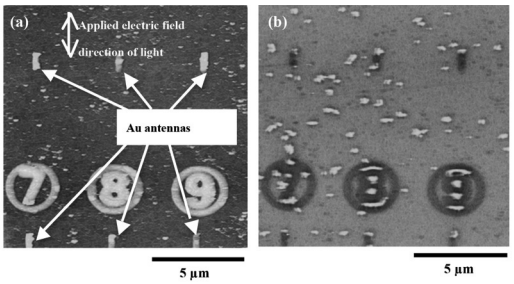


Fig. 6 Surface morphology (a) and written magnetic domains (b) observed by magnetic force microscope for rod plasmon antennas.

3) We found that the combination of dielectric optical waveguide and surface plasmon polariton is highly effective in optical energy transfer into small surface plasmon antenna. Besides, the combination structure can also create circularly polarized light in a small region.

4) A rapid thermal annealing is effective to obtain high Ku (uniaxial magnetic anisotropy) as well as small $L1_0$-FeCuPt grains. However, it revealed that each grain were mostly polycrystalline structure. We found that an application of adequate additional annealing makes grains into $L1_0$ single crystalline structures and grains kept almost similar size.

Collaborations and activities in 2012 as the group

A result about a nano-meter structured magnetic film with high uniaxial anisotropy was reported at an international conference (ICM2012, July 8-12, Pusan). At another international conference (ICAUMS2012, Oct. 1-5, 2012, Nara), six reports were also presented including femto-second laser thermally assisted magnetic recording, dynamics in first magnetic reversal, recording materials, and localized circularly polarized light. Some of these reports have been collaborated with Associate Prof. Ohnuki. We have kept an inner meeting at least once a month.

6. Advances and achievements in 2013

1) We found that all-optical switching with circular polarized femtosecond laser pulses in ferrimagnetic GdFeCo is related to the collinear sub-lattice magnetization and not with the net magnetization. Furthermore, we reached an explanation of the AO-HDS based on magnetic circular

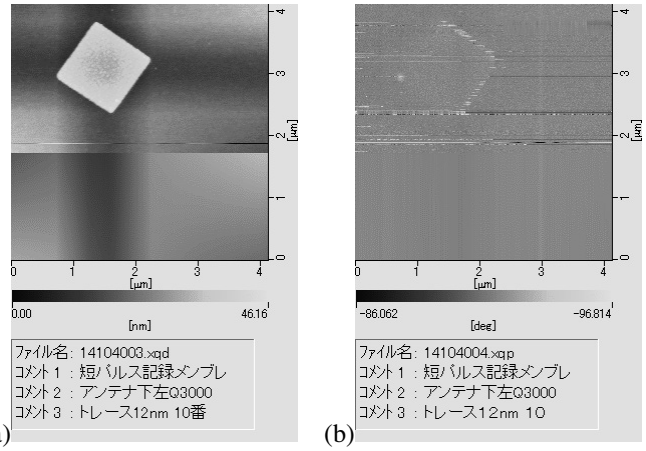
dichroism (MCD). We already reported that ultrafast heating can act as a sufficient stimulus for magnetization reversal in a ferrimagnet with taking into account the multi-sublattice nature as mentioned in section 5.1. The above results show that the helicity-dependent absorption in a multi-sublattice magnetic layer exactly matches the helicity-dependent features in switching experiments.
Furthermore, we clarified that the magnetization direction of high anisotropic magnetic recording media of TbFeCo can be switched by irradiation of circularly polarized ultra-short pulsed laser without magnetic field.

2) The minimum written domain size of 62 nm by 67 nm was successfully performed by femto-second laser utilizing surface plasmon antennas on magnetic film, beyond our final goal such as 77 nm by 77 nm.

3) It was revealed that a cross antenna, a cross aperture, and a four-leaf clover aperture can create a localized circularly polarized light applying with patterned media.

4) We started fabricating the cross aperture on Au metal by E-beam lithography.

5) From the utilization of self-assembly prepared nano-structured substrate, high density FeCuPt magnetic nano-grains was prepared by rapid thermal annealing method as 5.4 T particles/inch^{-2} with average grain diameter of ~10 nm.
Furthermore, multiple formation process of the grain was performed for further increase in areal density of grains. By using this procedure, we got higher areal density of grains as 3.2T particles/inch^{-2} on flat oxidized Si substrate.



(a) (b)

Fig. 7 Surface morphology (a) and written magnetic domains (b) observed by magnetic force microscope for square plasmon antennas.

Quantum Information Group

Takeshi Kuwamoto*, Hideomi Hashiba, Naoto Namekata

1. Overview of the research targets and plan

Purpose of research in quantum information group is to resolve technical problems for developing and expanding the quantum information, communication, and computer technologies, which are expected to achieve the large-capacity telecommunication beyond the conventional limit, the extreme high-speed calculation which far exceeds a supercomputer, and the ultimately reliable cryptography such that every eavesdropping and decoding are impossible in principle. Quantum information technologies can supply the system with very high energy efficiency, thus our research contributes to green innovation in information processing and communication.

We mainly investigated single photon emitter and detector, quantum key distribution, quantum memory, and quantum dot device.

2. Achievements of research

2.1. Photon Detection Technologies

Photon detector is essential for QICTs. In order to realize QICTs using installed optical fiber networks, the photon detector must have a high photon detection efficiency in telecommunication band (~ 1550 nm: the minimum-loss window of optical fibers) with low noise counts. We have developed the telecom-band single-photon detector (SPD) using a compound semiconductor device, namely an InGaAs/InP avalanche photodiode (APD). Although the SPD based on the InGaAs/InP-APD is very practical, it has drawbacks, compared with the other SPDs, that are an afterpulse noise and a low repetition frequency. We proposed a "sinusoidal gating" method in which a sinusoidal voltage was used as the gate voltage. Then, using the sinusoidally gated InGaAs/InP-APD, high-speed single-photon detection at 1550 nm can be realized with a low afterpulse probability. Currently, we achieved a repetition frequency of 2 GHz which is three orders of magnitude higher than that of the conventional gated InGaAs/InP-APD. Moreover, the photon detection efficiency of > 10% was achieved with a dark count probability of 10^{-7} and an afterpulse probability of < 3% (*IEEE Photo. Tech. Lett.* 2010; *Opt. Express* 2011). We also applied the sinusoidal gating method to a Si-APD. Using the sinusoidally gated Si-APD (quantum efficiency was 72.4%), visible-light single photons can be successfully detected with a detection efficiency of 70.6%, which implies that a photo-excited single charge carrier in a silicon avalanche photodiode can trigger a detectable avalanche (charge) signal with a probability of 97.6% (*Appl. Phys. Lett.* in press).

Although advanced QICTs demands the photon number resolving capability, the SPDs described above do not have it. Therefore, we have developed the so-called photon-number-resolving detector (PNRD) using a superconducting Titanium transition edge sensor (Ti-TES). We achieved a detection efficiency of > 80 % at 1550 nm with a photon number resolving capability of < 0.2 eV. Then, we applied the developed PNRD to a non-Gaussian operation on the pulsed squeezed vacuum at 1550 nm. The two-photon-subtracted squeezed state was successfully generated (*Nature Photonics*, 2010). We observed dips in reconstructed Wigner functions of the generated

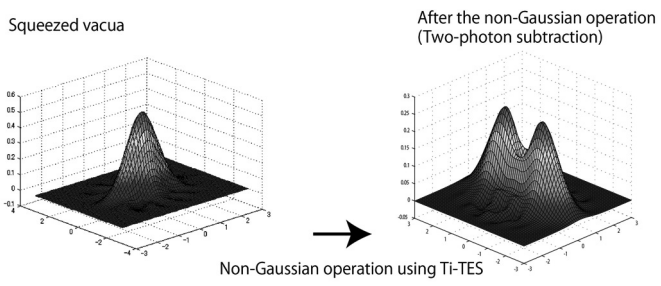


Fig. 1. Wigner function of the generated non-Gaussian state

quantum states (see Fig. 1), which is the clear evidence that the non-Gaussian operation was realized.

2.2. Quantum Key Distribution Experiments

We performed a 2 GHz clocked differential-phase-shift QKD (DPS-QKD) experiment using SPDs based on sinusoidally gated InGaAs/InP-APD. A secure key rate of 24 kbit/s was achieved over 100 km of optical fiber, which was higher than the previous record. Moreover, we have successfully distributed secure keys against the general individual attacks over 160 km of optical fiber (*Opt. Express*, 2011). These results will accelerate the realization of a practical QKD over a metro-sized optical fiber network.

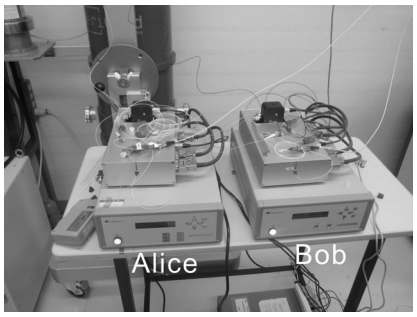


Fig. 2. Entanglement-based QKD

To extend the communication distance further, e.g. > 400 km, entanglement-based QKD system is preferable, because it will play an important role in the quantum repeaters described in the next section. We have developed the polarization entangled photon pair source and the entanglement-based QKD system using it (Fig. 2).

2.3. Elemental Technologies for Quantum Repeater

To realize the long-distance QKDs, we need the quantum repeater which can improve the throughput reduction with distance from exponential to polynomial. The quantum repeater is composed of three elemental technologies: the entanglement swapping, quantum memories (or buffer storages), and the quantum non-demolition measurement of the photon number.

We demonstrated entanglement swapping with 1550 nm polarization-entangled photon pairs created by spontaneous parametric down conversion (SPDC) in two spatially separated type-II periodically poled lithium niobate (PPLN) bulk crystals. In a partial Bell-state measurement, entanglement was observed between two photons from independent sources. We employed sinusoidally gated InGaAs/InP-APDs operated at a repetition frequency of 1.28 GHz, which increased a four-fold coincidence count rate without degrading the fidelity of entanglement swapping. The obtained fidelity is ~ 90% which is high enough to infer a violation of Bell inequality and to implement the entanglement-based quantum key distribution (*J. Phys. B*, 2013).

In our experiment, the success probability of the entanglement swapping is less than 10^{-6}. To enhance the success probability, the key technology is the quantum memory (or buffer storages). In this work, we have tried to realize the photon buffer storage by means of an optical switching network. As shown in Fig.3, the photon buffer storage we designed is composed of optical fibers and low-loss fiber-optic components. It gives the programmable optical delay to photons with a low optical loss, and a quantum state of light (polarization of photons) can be maintained without any active compensation.

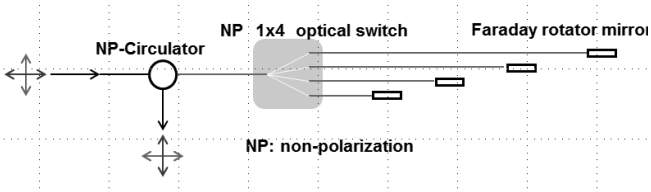


Fig. 3. Photon buffer storage using the optical switching network.

2.4. Development of quantum memory

2.4.1. Generation of orthogonally polarized photon pairs

Quantum entanglement states are made up of orthogonally polarized photon pairs. Atomic sample we use is ^{87}Rb atom, and its transition wavelength for photon storage is 795 nm with linewidth of 6 MHz. Therefore, we have to prepare the orthogonally polarized photon pairs which met above

requirements.

Orthogonally polarized photon pairs with 795-nm wavelength were produced by a parametric down conversion which was brought about by injecting a 397.5-nm-wavelength pump laser into 10-mm-length nonlinear optical crystal (type II PPKTP). The pump laser was obtained by pumping a type I PPKTP crystal placed in a bow-tie type optical resonator with a 60-mW power, 795-nm-wavelength laser. Orthogonally polarized photons immediately after the crystal have the frequency expansion of THz order. Since the bandwidth of photons coupled with atoms is several MHz, this wide spread of frequency have to be narrowed. We utilized optical interference filters and etalons to obtain the narrow-bandwidth orthogonally polarized photons.

Figure 4 shows result of two-photon interference measurement of generated orthogonally polarized photon pairs. This measurement is performed to estimate quantum property of the photon pairs. The obtained visibility was 97.4%. This result shows that generated orthogonally polarized photon pairs satisfy a demand as the quantum light source.

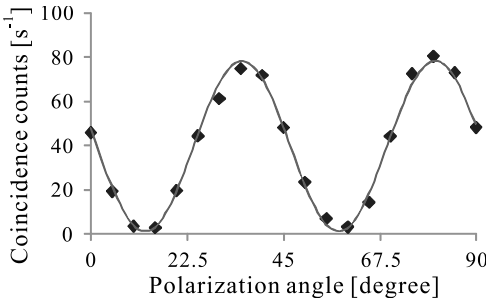


Fig. 4. Two-photon interference of orthogonally polarized photon pairs.

We measured the absorption of the generated photons by ^{87}Rb atoms to confirm the frequency extent of photons. At the temperature of 95°C, 97% of photons were absorbed. This means that the frequency broadening of photons is about 500 MHz.

2.4.2. Light Storage system

The phenomenon called electromagnetically induced transparency is used to store the light in neutral atoms. When two different resonance lights are shined to three level atoms, by controlling the intensity of one light (control light), the other (probe light) can be stored in atoms. We used ^{87}Rb atoms enclosed in grass cell as the sample, because of the abundant knowledge of its properties.

As probe and control light source, two external cavity diode lasers were used. The frequency fluctuation of control laser was controlled by a frequency locking system using Rb sample, and suppressed to be less than 1 MHz. The frequency of probe laser was controlled by the optical phase-lock with the beat signal between the probe and control lasers such that the frequency difference between two lasers agrees with that between the two low-lying atomic-energy levels. The probe laser beam was formed to a 5-μs-width gaussian pulse with an acousto-optic modulator. Rb sample grass cell was placed in a threefold magnetic shield and its temperature was controlled with a heater using hot-water.

The probe and control laser beams were coaxially propageted and injected into the Rb grass cell. By suddenly switching off the control laser light, the probe light pulse was stored in the atomic sample. Figure 5 shows an example of results of light storage experiment for the storage time of 5 μs. The efficiency of retrieved light pulse was 85%. This value means that we prepared sufficiently high-performance experimental system for light storage.

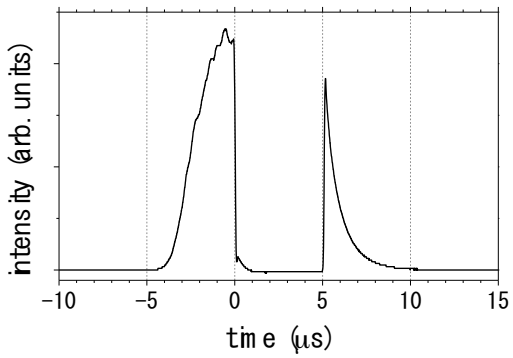


Fig. 5. Result of storage and retrieval experiment for laser pulse. The right peak corresponds to the retrieved light pulse after 5-μs storage.

We investigated the storage of extremely weak coherent light pulses, because the intensity of orthogonally polarized photons would be very weak. The retrieved signal was not confirmed for the 2.6-nW probe laser power. This means

that the storage and retrieval of orthogonally polarized photons using current our system is difficult.

2.5. Development of fabrication technology of silicone waveguides, Au strip couplers and single photon emitters by one dimensionally aligned CdSe quantum dots

Semiconductor wave guides and photonic crystals are increasingly important in optoelectronic devices for quantum information technology. We study silicone wave guide devices with its third-order nonlinearities. Research of silicone wave guide devices on this project has been focused on development of simple fabrication method of the waveguides and we attained to develop concrete fabrication method for a Si waveguide of 320 nm wide and more than 1 mm long. The waveguide has small roughness of side-walls of less than 10 nm and accuracy of shape of the waveguide is restricted by our EBL that has field alignment precision of around 100 nm by auto-align mode or around 50 nm by manual align. This also affects for large sized structure such as Au stripe couplers. We also studied fabrication technique of arrays of colloidal quantum dots of 5 nm CdSe covered by silica. We attained 55 nm wide, 1.5 mm long array of the QD in sub-one dimensional shape. Evanescent coupling of the quantum dots to gold thin film of 37 nm was also confirmed.

2.6. Fabrication of titanium dioxide photonic crystals for dye sensitized solar cells

Titanium dioxide (TiO_2) has been draw attention for dye sensitized solar cells by its catalytic characteristics. Our aim is an experimental study of fabrication of fine structures, i.e. photonic crystals, of TiO_2 for solar cells to enhance its efficiency. A TiO_2 thin layer of 150 nm thick was grown on an FTO glass substrate with a fine patterned ZEP resist mask by a conventional RF magnetron sputter method with Ti target (upper of Fig. 6). We found that, during the deposition, keeping ratio of Ar-O_2 gas of 2:1 and the deposition ratio of around 0.5 Å/s ensures enough oxygen to form TiO_2 and low temperature to avoid deformation of fine pattern of the ZPU resist mask. Design of the fine patterns is photonic crystal structure of periodic zigzag slabs of 108 nm width, 608 nm in period. TiO_2 layers are white-transparent, amorphous, and those roughnesses are around 7 nm. Baking of TiO_2 fine structures at 500 ºC transforms TiO_2 from amorphous to rutile and anatase forms while keeping the same profile of the fine structures (lower of Fig. 6). Our new fabrication method can be one of a promising technique to optic devices on researches and industrial area.

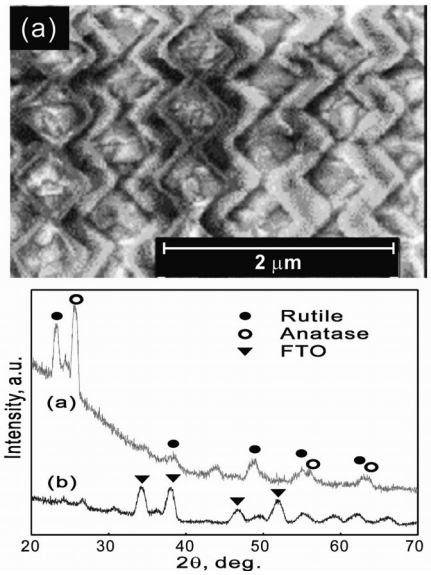


Fig. 6. (upper) TiO_2 photonic crystal. (lower) XRD measurement of TiO_2 after baking. Rutile and anatase appeared.

3. Collaboration and activities as the group

We had several times of group meeting every year to report and share individual progress, and discuss the direction of research. We also collaborated with Prof. Ohtsuki and Prof. Ohnuki about the development of a multichannel single-photon device which composed of CdSe colloidal quantum dot array and plasmonic waveguide.

Energy Technology Group

Takuya Hashimoto,* Joe Otsuki, Sachiko Matsushita, Yasuo Asada, Nobuyuki Nishimiya

1. Purpose

Development of materials, which will construct new energy system, has been performed toward "Construction of Healthy Society" under the common keyword, "nano" in the energy group. For realization of "Healthy Society", enough energy supply is highly required; however, practically employed energy systems contain severe problems. Mainly employed fossil fuel system involves anxiety for depletion of resources and exhaust of greenhouse gas. Nuclear energy system has possibility of destruction of environment and human health as revealed by accident of nuclear plant at Fukushima prefecture.

In this project, in order to construct solar energy system which is free from above mentioned anxieties, the following researches have been carried out. (1) Development of dye-sensitized solar cell using "nano-structured electrode" or materials with "controlled molecular structure", which is one kind of nano structure. (Matsushita, Otsuki) (2) Development of H_2 generation processes using direct H_2O photolysis, which are clean energy processes with absence of greenhouse gas emission. One approach is development of catalyst materials with controlling molecular structure, so-called artificial photo synthesis. (Otsuki) The other one is usage of bacteria which generates H_2. (Asada) (3) Development of new hydrogen-storing alloy by nano-space design for safe transportation and storage of H_2. (Nishimiya) (4) Development of materials for solid oxide fuel cells in order to realize clean electrical generation using H_2 as resource gas. Synthesis of high functional materials is examined with Pechini method, which is one of nano-processes. (Hashimoto) Fig. 1 shows schematic diagram of final purpose of the energy group. We regard that technology of each research should be sophisticated for high correlation of each research.

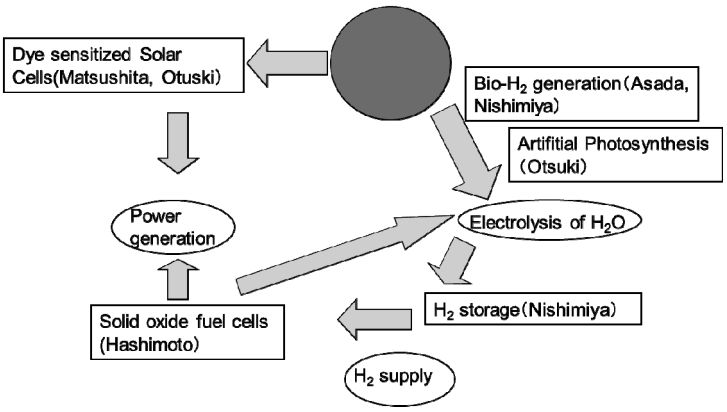


Fig. 1 Schematic diagram of purpose of energy group. Red circle represents sun.

2. Plans, progress and achievement of energy group

Abstracts of each research are shown here. Minute reports are presented in each researcher's report.

(1) Improvement of energy conversion efficiency of dye-sensitized solar cell by using nano-structured electrode. (Matsushita)

It has been suggested that energy conversion efficiency per one molecular dye is improved by employing "self-organized" photonic crystal as electrode in the dye sensitized solar cell. In order to clarify the effect of photonic crystal, micro patterning of TiO_2 is highly required. In this project, technology of photo- or electro- lithography of TiO_2 has been established and experiments of verification of role of photonic crystals have been prepared.

(2) Improvement of energy conversion efficiency by development of new dye. (Otsuki)

Development of new dye for improvement of energy efficiency of dye sensitized solar cell has been investigated. Complexes composed of Ru and perylenedicarboxylic anhydride derivatives have been examined and conversion efficiency of 3.1 % has been realized. In addition, preparation of new promising cyclometalated complexes has been succeeded and investigation of their property as dye sensitized solar cell materials is in progress.

(3) Development of new catalyst for photolysis of H_2O (Otsuki)

As a new catalyst for photolysis of H_2O, molecular in which the photosensitizers spontaneously assemble around cobalt ion has been prepared. Amount of H_2 produced by illumination using this catalyst was as twice large as one produced without self-assembly.

(4) Improvement of amount of H_2 generation from bacteria by addition of encapsulated H_2 storage alloy (Asada, Nishimiya)

It is well known that some kinds of bacteria generate H_2 gas by H_2O photolysis. In this project, it has been revealed that addition of encapsulated H_2 storage alloy to the H_2O photolysis system employing bacteria is effective to increase amount of H_2 generation.

(5) Control of H_2 storage and desorption of metal alloy with ultraviolet light irradiation (Nishimiya)

For H_2 storage metal alloys, not only large amount of storage but also ability for easy H_2 desorption are required. In this research, it has been discovered that H_2 storage and desorption property in some metal alloys can be controlled by irradiation of ultraviolet light. Especially in the presence of photo-catalyst such as WO_3, H_2 desorption temperature has reduced by ultraviolet light irradiation.

(6) Development of catalytic metal for decomposition of H_2 (Nishimiya)

For increase of amount of H_2 storage by adsorption on the solid surface, decomposition of H_2 to H atom is effective. In this project, various metals have been surveyed as for metal catalyst for decomposition of H_2 at temperature of 77 K, at which adsorption on the solid surface occurs. It has been revealed that Pt is the most promising and that Cr-Fe alloys has high potential as catalyst.

(7) Development of materials for intermediate-temperature solid oxide fuel cells. (Hashimoto)

At present, solid oxide fuel cells, which is free from emission of greenhouse gas and has high energy conversion efficiency, works above 800 ºC, resulting in less reliability and practical stability. For reduction of operating temperature to 600 ºC, development of new materials has been examined. In this project, one of the solution mixing process, Pechini method, was employed for the preparation of materials instead of conventional solid state reaction method. Owing to nano-level mixing, we have succeeded in preparation and proposing new materials as electrolyte and electrode. Test cells are fabricated and investigation of their property is now in progress.

3. Collaboration in energy group and with other research group

Not only collaboration in energy group but also that with other research group have successfully been carried out.

Achievement listed in (4) is a collaboration work between Prof. Asada, who is a specialist of biology, and Prof. Nishimiya, who is a specialist of H_2 storage alloy. The addition of H_2 storage alloy to biologically H_2 generation system has been patented. Investigation of dye-sensitized solar cells composed of photonic crystals has mainly been carried out by Prof. Matsushita. Prof. Hashimoto made collaboration on the work using X-ray diffraction and SEM measurements. The collaboration was presented by two academic papers published in “J. New Mat. Electr. Sys.” and “J. Porous Mater.”

The success of establishment of technology of photo- and electro-lithography is due to collaboration between Prof. Matsushita and Prof. Hashiba, who belongs to nano-group in N. Research Project. The collaboration is published as academic paper in Jpn. J. Appl. Phys. The Pechini method, employed for fabrication of new material for solid oxide fuel cells by Prof. Hashimoto, is also applied for fabrication of target materials for thin film fabrication by Prof. Iwata, who belongs to nano-group. It has been clarified that superior ceramics not only as solid oxide fuel cells but also as target for thin film preparation can be prepared by the Pechini method.

Medical Group

Medical Group Members

ARISH: Fukuda N, Chiba Cancer: Nagase H, Watanabe T, Nihon Univ. School Med. Severe Disease G: Soma M, Fujiwara K, Saito K, Igarashi J, Radiology: Abe O, Abe K, Urology Takahashi S, Pediatric Surgery: Koshinaga S, Nihon Univ. Bioresourse Science: Masuhiro Y, Kano K, Nihon Univ. Pharmacy: Matsumoto Y, Aoyama T

Ishibashi N, Kawashima H. Shinojima Y, Hasegawa R, Mashiko A, Oh G.

Research Summary

Medical Group has performed researches in two themas as "Applied chemical biology: strategy to cure cancer patients" to develop novel diagnosis methods for cancer using nano thechnology in corroboration with Chemical group in Colledge of Science and Thechnolgy, and as "Drug-discovery for novel gene silencer pyrrole-imidazole polyamides" for cancer and sever diseases based on the chemical genomics.

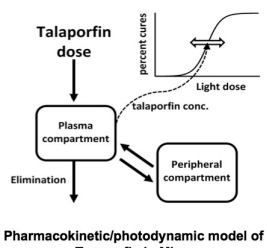
Contents of Researches

1) Novel chemosensitizing radiation therapies by using synthetic porphyrin derivatives (Nagase, Fujiwara, Soma).

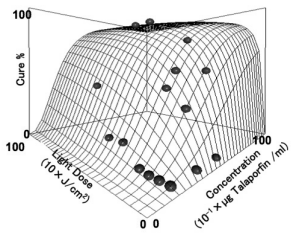
Photodynamic therapy (PDT) is a medical treatment that uses a photosensitizing chemical and a light source to activate the applied chemical. The result is an activated oxygen molecule that can destroy nearby cells. Precancerous cells and certain types of cancer cells can be treated by PDT. Cancer cells uptake more of the porphyrin derivatives and retain the chemicals in a long duration. Thus, the PDT can introduce a cancer cell specific therapy. We invented the radiation-sensitizing chemical of the porphyrin derivatives, which can be used for PDT and may also induce photon activation therapy (PAT), provoking the emission of Auger electrons after inducing a photoelectric effect. X-ray radiation allows for the treatment of cancers that are deep inside the human body. We observed an induced cancer cell death after irradiation following administration of the porphyrin derivative.

2) Pharmacokinetic/Pharmacodynamic Analysis of tumor-localizing photosensitizing compounds (Matsumoto, Aoyama)

To describe the relationships between effects following photodynamic therapy, light dose, and plasma compound concentration, they developed a high-performance liquid chromatography (HPLC) method for the determination of plasma concentration and investigate the pharmacokinetics of novel compound CT101019a.



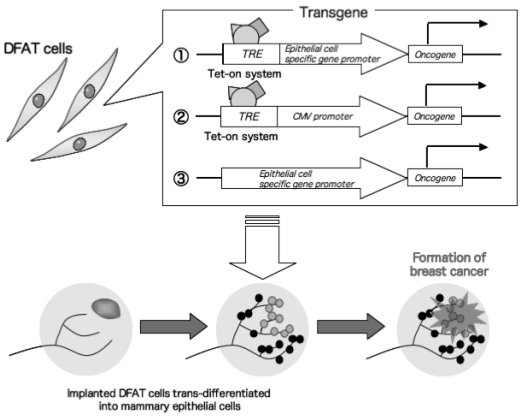
Pharmacokinetic/photodynamic model of Taraporfin in Mice



Simulated curvilinear surface between percent cures, light dose, and talaporfin concentration

3) A novel model of onset breast cancer by implanting mature adipocyte-derived dedifferentiated fat (DFAT) cells (Kano K)

To develop a breast cancer mouse model, mouse DFAT-GFT cells were transfected with protooncogene to transform to the mammary epithelial cells by the conditional regulation of the gene expression. Using the mouse breast cancer models, we demonstrated introduction of the cancer cell death with increasing sensitivity to radiotherapy with developed the PDT.

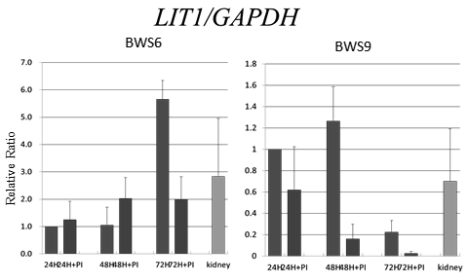


4) Development of an E-box targeting Pyrrole-Imidazole polyamide to inhibit cell growth (Fujiwara, Soma)

PI polyamides targeting E-box consensus inhibited proliferation of the osteosarcoma cell line treated with Myc-6 showing reduced growth rate by WST8 assay and colony formation assay. In the wound-healing assay, Myc-6 inhibited cell migration activity dose-dependently. Intravenous injection of Myc-6 once a week for a month caused growth inhibition MG63 xenograft developed in Nude mouse without evidence of toxicity.

5) Development of antitumor PI polyamides for pediatric cancer (Koshinaga)

PI polyamides（h-CCAAT1, h-CCAAT3）designed on the CAAT box in promoter reasion of LIT1 gene efficiently suppressed expression of LIT1 gene and proliferation of Hepatoblastoma cell line (HuH6 clone5, HepG2), and Wilm's tumor cell line (G401).



6) The development of newly molecular targeting drug of PI polyamide for prostate cancer (Takahashi S, Obinata)

Human prostate cancer cell line treated with Fusion Polyamide was compared with those with Negative control polyamide. Treatment of Fusion Polyamides showed significant decreased both DHT induced TMPRSS2-ERG and endogeneous ERG expression, as well as cell growth and migration. These results demonstrate that PI polyamide targeting these breakpoints sequences may be a new therapeutic intervention in prostate cancer. We confirmed anti-tumor efficacy of the PI polyamide in the animal experiment using a nude mouse in vivo.

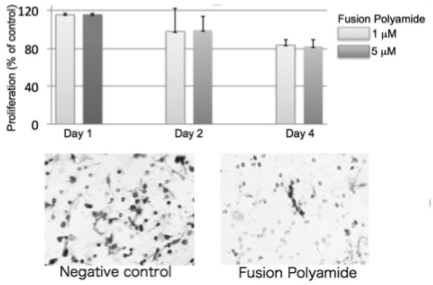
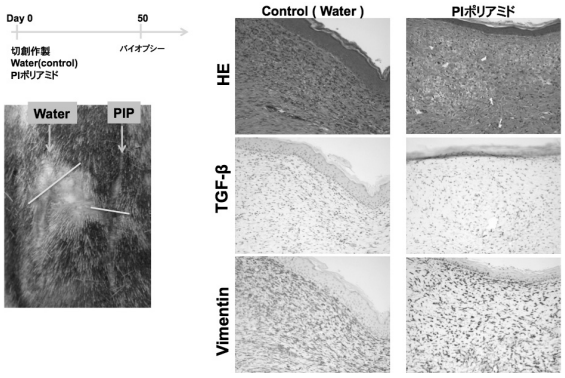


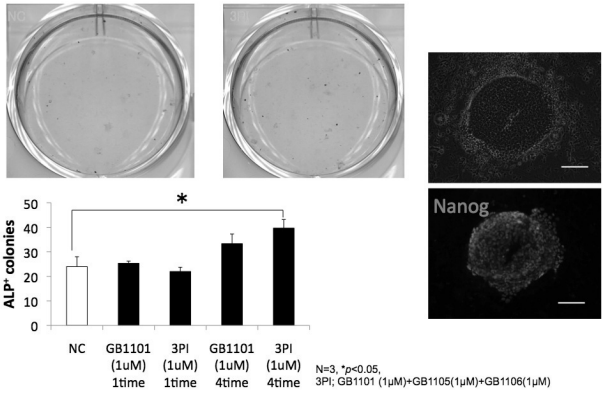
Fig.2 Effect of fusion polyamide on cell migration and anchorage-independent growth. Cell migration assay was performed to analyze the motility of fusion polyamide treated LNCaP cells and control cells. Migrated cells were stained with Giemsa staining solution

7) Development of PI polyamide targeting human TGF-β1 -Preclinical study- (Igarashi, Fukuda):



We confirmed that PI polyamide targeting human TGF-β1 (GB1101) is strongest to inhibit the expression of TGF-β1 mRNA in human- and marmoset-derived fibroblasts. We checked the combination of components of soluble materials and solutions for PI polyamides and found that Macrogol Ointment was most effective substrate to delivery the PI polyamide into skin. We examined effects of PI polyamides targeting human TGF-β1 on development of skin finrotic scar created in common marmosets and confirmed acual inhibition of the skin scar.

8) Development of the Nihon University original methodology inducing iPS cells using the PI polyamide targeting human TGF-β1 (Saito, Fukuda, Masuhiro)

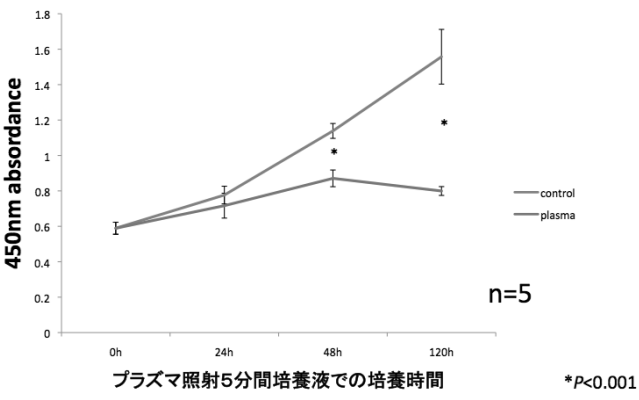


We examined the iPS-producing method establishment using proteolysis resistant cell-permeable proteins and the iniciation factor, TGF-β1 inhibitor, PI polyamide targeting human TGF-β1, Apigenin, TGF-β1antagonist and Apigenin, and TGF-β1 and PI polyamide targeting human TGF-β1.

9) Histone acetylation of specific genomic region induced by PI polyamide-SAHA conjugate (Nagase, Watanabe)

We made considerable advances in coupling of existing drug SAHA that is begin used as an HDAC inhibitor, to PI polyamides for targeting specific subsets of genes for reactivation in cancers (e.g. Cdkn2a / p16). Watanabe developed a method of simple synthesis with solid phase synthesis method using glutamic acid which is the usual amino acid. Six ring cyclic PI polyamide was synthesized.

10) Development of plasma medicine for skin malignant melanoma (Saito, Fujiwara, Fukuda)



We started a project of the development of plasma medicine for skin malignant melanoma collaborating with the plasma team in College of Science and Technology. This plasma medicine targets the cancer stem cell with all trans retinoic acid to reduce the tolelance of radical oxygen species.

Activities of Medical Team in 2013

1. Meeting of N. Research team in every week.
2. Meetings in the collaborating institute Central Institute for Experimental Animals Common marmoset team for the development of PI polyamide targeting TGF-β1.
3. Meeting with the Drug Preparation Room in Nihon University School of Medicine Itabashi Hospital and Clinical Pharmacokinetics team in College of Pharamacy about the development of PI polyamide targeting TGF-β1.
4. Meeting with the team in College of Pharamacy about the GLP grade phamakokinetics study for PI polyamide targeting TGF-β1.
5. Meeting for the development of plasma medicine for skin malignant melanoma collaborating with the plasma team in College of Science and Technology.
6. Presentation for the development of PI polyamide as practical medicine in College of Pharmacy.

Supramolecules and Self-Assembly Group

Hiroki IKAKE,* Akiyoshi ITOH, Joe OTSUKI, Arata TSUKAMOTO, Sachiko MATSUSHITA

1. Introduction

The goal of the supramolecules and self-assembly group is to develop advanced technologies on nanomaterials and nanostructures and to supply these technologies to the application-oriented groups, *i.e.*, the information, energy, and medical groups, thus strongly promoting networking among these groups on diverse fields. As follows, each groups theme in this project for 5 years.

2. Research Project on each group for 5 years

・ The development for super high density memory device (Itoh & Tsukamoto Group)

By using the self-organization/integration phenomena of the polymeric micelles,we produced a fine substrated silica particles, which were regularly arranged three-dimensionally (Fig.1). We started the development of a template to obtain a nanostructured metal material by using this substrate. And then, we were obtained this template (Fig.2). In this study, we discussed to produce a FeCuPt ordered alloy particles. In the super high density recording, it was not only the particle size of the magnetic particles, the magnetic axis (c-axis) was perpendicular to the surface of film and a single crystal of regularly $L1_0$ phase was necessary. We could be produced the single crystal FeCuPt nanoparticles of c-axis oriented by rapid heating heat treatment. In addition, we obtained magnetic nanoparticles completely isolated number density was 5.4T particles/inch^{-2}. Furthermore, we carried out a plurality of the process, and then we obtained the nanoparticles, which were the average particle diameter of about 10nm and the number density of about 3.2T particles/inch^{-2} in Si substrate.

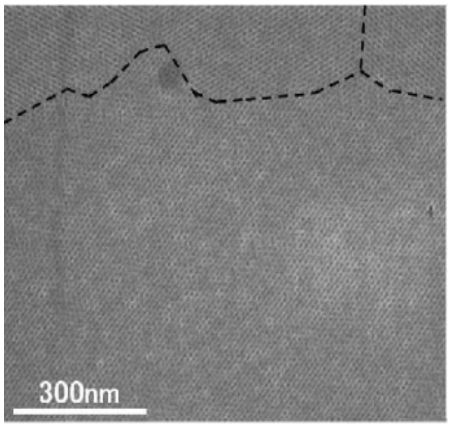


Fig.1 SEM imaging of fine silica template.

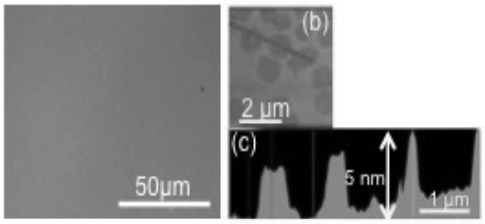


Fig.2 SEM and AFM images of fine silica template.

・ The development of light and quantum function of nano-molecular systems using self-assembly phenomenon (Otsuki Group)

We have succeeded in visualization of the motion of a single molecule by using STM (Fig.3). We made attempts to prepare a regularly arranged two-dimensional nano-structure as a single photon source, in which the distance between quantum dots is greater than visible wavelength. We have found that pyridine-appended chlorophyll molecules form double helical structures, which was revealed by the single crystal X-ray crystallography, reminiscent of the double helices of DNA. While an oxazole-appended chlorophyll derivative leads to a stair-case type architecture. These works constitute a step toward constructing artificial antenna systems based on molecular assemblies. We have also synthesized new metal complexes as a sensitizer for dye-sensitized solar cells.

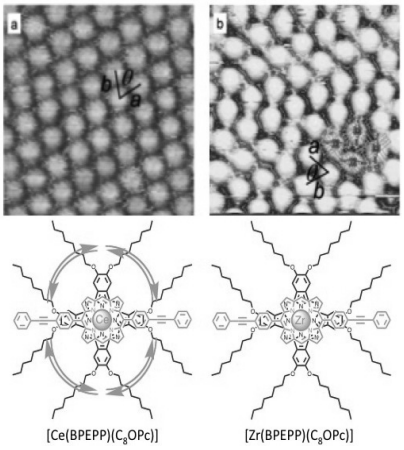


Fig.3 Visualization of the rotational motion of the molecule.

・ Preparation of the optical device by using nano-particles with self-assembled and photonic crystal (Matsushita Group)

Our group aimed to the construction of optical devices by using photonic crystals, and we have discussed the photoelectric conversion efficiency, and we have studied the relation to lifetime of electrons and the interface of device. We have prepared the regular structure necessary for plasmon control in the visible light region by using the self-assembly / integration behavior, to which has a three-dimensional dense aggregate such as silica, and then we could be produced fine particles, which was etched by using hydrogen fluoride aqueous solution (Fig.4).

Further, We had found the titanium oxide - the electrolyte photonic crystal with having full-photonic-band gap and complete-photonic-band gap by using two-dimensional expansion method. Indeed, we incorporated into the calculated result the wavelength dispersion of the refractive index of titanium oxide as factor, and then we could create a new photonic band diagram and were able to have versatility on the operation result. We prepared single crystals of titanium oxide by using the calculation results, and then we were obtained its photonic band diagram by reflection spectroscopy method. From these results, we have prepared a regular structure with having a complete-photonic-band gap, in order to confine the light completely in a two-dimensional plane as a novel inhibiting emission photonic crystal. We have revealed that the crystal structure in the dye-sensitized solar cell incorporating its photonic crystal was related to the photoelectric conversion efficiency of per one-photon and per one dye.

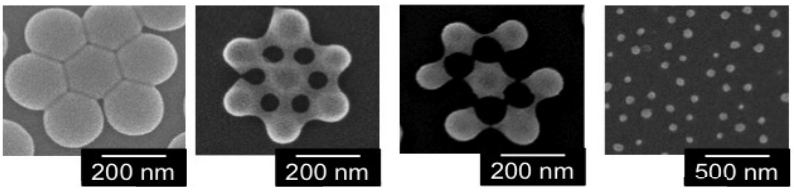


Fig.4 The isotropic etching by using an aqueous solution of hydrogen

・ Development of Poly(lactic acid)s Films as biopolymer, and Applications to New Material Field (Ikake Group)

Our group attempted the preparation of poly(L-lactic acid) (PLLA) oriented film as a novel optical material by using PLLA, which is crystalline polymer, with having a biodegradable function. In this study, we have prepared the PLLA films under the magnetic field of 10T. We have revealed that the degree of crystallinity and orientation of PLLA film is facilitated by controlling the heat treatment conditions and irradiation of magnetic field in this process. We discussed the relationship between the azimuth angle of PLLA films and the intensity of transmitted laser of these films by using He-Ne laser (wavelength 632.8nm). As a result, we have found the polarizing properties of these films by the periodic changes of the laser intensity. Next, we have prepared an optical film with using sc-PLA, which including stereocomplex crystal formed from PDLA of different chirality and PLLA. Sc-PLA has excellent properties, heat resistance and mechanical strength, compared to PLLA, and we could control the size of the stereocomplex crystal of films, in which formed sc-PLA films by using casting solvent. As shown in Fig.5, in the case of use 1,4-dioxan as solvents, the films became opaque due to the increasing size of stereocomplex crystal. On other side, in the case of chloroform films were transparent due to become small crystal size in film, and the film has the transmittance to 85% in visible light region of 400 ~ 800nm. In addition, we also discussed that sc-PLA film recycling for after use. We have prepared sc-PLA / silica hybrid materials by using the sol-gel method. Silica hybridized by nanometer size inside the films, and these hybrid films have high heat resistance than the sc-PLA film, and also showed a rubber plateau behavior in the high temperature region.

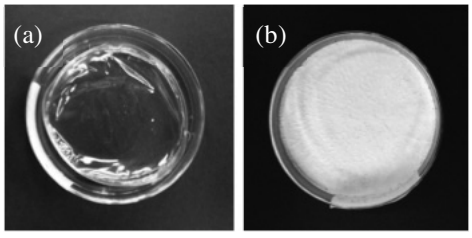


Fig.5 Appearance of (a) mix-PLA(CHL) and (b) mix-PLA(DOX) films.

Nanomaterials and Nonodevices Group

Kaoru Suzuki*, Yoshiki Takano, Tomohiko Asai, Nobuyuki Iwata, Hideomi Hashiba, Shigeru Chaen, Ken Judai, and Shosuke Mochizuki

Purposes

This group aims at fabrication of nanomaterials and nanodevices for high functional applications such as electric circuits, biosensor, superconductors, EUV light source, field effect transistor, quantum dot terahertz single photon detector, solid oxide fuel cells, new photo-memory, and bio-nanomotor by using fundamental techniques of nano-process, fabrication of nano-materials, analysis of nano-level structure and analysis by nano-technique.

Plans

Prof. K. Suzuki : Carbon nanotubes (CNTs), nanorod (CNR) and nanofibers (CNFs) have attracted great interest due to their novel electrical, optical, and mechanical properties. These materials are promising candidates for a large variety of nanodevices, such as electric circuits, biosensors, and optical components by wide band gap, Eg(carbon)>5.6 eV, semiconductor effect. CNR and metal included CNTs are now sometimes grown on a silicon substrate with metal catalyst through thermal decomposition in ethanol at temperatures from 973 K to 1273 K by joule-heat with a DC power supply. The hydrogen yield on water decomposition with the lanthanum doped titanium dioxide thin films on quartz substrate that apply the photo catalytic reaction have been studied for fuel cell by using plasma assisted pulsed laser deposition method with non-sintered heavily La doped TiO2 target.

Prof. Y. Takano: Since the discovery of high T_c superconductivity in $(LaO_{1-x}F_x)FeAs$ in 2008, many researches on the iron-based superconductors have been carried out. Before this second superconductivity fever, it was reported that (LaO)FeP became superconducting at about 4 K. However, several research groups reported different T_c in (LaO)FeP. Thus, the electrical properties of LaOFeP is still controversial. Takano has considered that the stoichiometry of the sample is important to determine the electrical properties. Then, he has prepared single phase samples of $La_{1-x}OFeP$ using the special heat treatment and measured their structural, electrical and magnetic properties.

Asso. Prof. T. Asai is studying the application of self-organized magnetized plasmoid. His research interest is experimental physics and application self-organized magnetized plasmoid. In this project, he is focusing on application of the compact toroid which has been less applied so far. Currently, his experiments are focusing on development 1) EUV light source and 2) alloy-film generation. Both are realized by exquisite control of discharge on magnetized coaxial plasma gun using high-power IGBT inverter developed in our lab.

Asso. Prof. N. Iwata is studying : i) The SWNTs were grown by alcohol chemical vapor deposition (ACCVD) method on quartz substrate with Co/Mo catalysts. In order to grow SWNTs with specific chirality, free electron laser (FEL) was irradiated during growth. ii) Gold (source and drain electrodes) sputtered SiO_2/Si substrate was dipped with a speed of 1mm/s from C60 saturated toluene solution. In advance of the dipping, the surface of the substrate and Au electrodes was treated into hydrophilic or hydrophobic. iii) A ferromagnetic domain can be controlled by a spin direction of Cr ion at the interface in ferromagnetic metal / Cr_2O_3 multilayer. Considering a magnetoelectric effect of Cr_2O_3, the ferromagnetic domain is controllable by a electric field applied to the Cr_2O_3. Single crystal Cr2O3 thin film is required for the ferromagnetic domain controllability. iv) LaFeO3(LFO)/CaFeO3(CFO) superlattice was grown by pulsed laser deposition (PLD) method. The superlattice was alternate growth of 7 units of CFO and LFO, and that was repeated for 14 times.

Assis. Prof. H. Hashiba is studying TiO_2 photonic crystal embedded on quantum dot terahertz single photon detector. An experimental study of a sensitive detector for terahertz radiation, based

on a GaAs/AlGaAs quantum dot (QD) of ~1 micrometer size defined by mesa patterning and metal gates has been reported. Quantum efficiency of the absorption of individual photons, inducing a charge polarization of the QD, is enhanced by an introduction of photonic crystal. He developed 2-dimensional TiO_2 photonic crystal fabricated by standard electron beam lithography for the detector. The photonic crystal is designed to have full band gap energy around a wavelength of incoming photons. This project aims enhancement of the efficiency of the detection and selectivity of polarization of incoming photons.

Prof. S. Mochizuki : The photoluminescence properties of different pristine CeO_2 specimens (bulk crystal, film and nanocrystals) have been firstly studied at different temperatures between 7 K and room temperature. The photo-induced luminescence spectral change has been observed at room temperature for the first time. The phenomenon observed in a vacuum is explained as a photo-induced associative detachment of O_2 on the specimen surface, while that observed in O_2 gas is explained as a photo-induced dissociative adsorption of O_2 on the specimen surface.

Prof. S. Chaen : We have constructed expression vectors for 4 kinds of long-wavelength shifted fluorescent proteins. In vitro single molecule imaging of these proteins fixed on a cover glass has been conducted. Each protein exhibits distinctive characteristics upon fluorescence intensity and photo-breaching resistant properties.

Asso. Prof. K. Judai is interested in a chiral nano helix assembled from achiral molecules. The process, the origin of chirality and the control of nano helical structures were investigated.

Progresses

Prof. K. Suzuki has performed the following studies.

(1)Metal encapsulated carbon nanotube for magnetic force microscope probes: The diameter and length of the Ni filled CNT were in the range of 10 – 80 nm and 100 – 800 nm with varying heating period and temperature, respectively. The walls consist of cylindrical graphene sheets with 3 -50 layer. The structure of synthesized stainless-steel filled CNT processes 3 phases which indicate that monocrystal of Fe2(1-x)Cr2xO3 in A part, polycrystal of Fe2(1-x)Cr2xO3 in B part and monocrystal of Fe(1-x)Crx in C part by NBED analyses.

(2)Creation of carbon nano-tube/rod and diamond-like carbon devices: Carbon nano-tube/rod forests were closely grown, one of a CNT was processed by focused Ga+ ion beam. Voltage and current characteristic shown diode property

(3)Synthesize of photocatalytic SrxLa1-xTiO3 film for hydrogen generation: La doped TiO2 have attracted great interest for photocatalytic properties, which can be used visible area in solar light although only TiO2 limiting with ultra violet area.,and deposit of TiO2 on polymer films by laser induced forward transfer method. A magnetized coaxial plasma gun is utilized for a deposition of high-melting-point metal such as Ti0.5Zr0.5(Fe0.2Mn0.8) for hydrogen storing alloy collaborative study with prof.Nishimuya and Asai.

(4)Synthesis of ZnO nano-films for light emitting device: We have synthesis nitrogen doped p-type ZnO nano-films by infrared light excited pulsed laser deposition method. High quality crystalline of p-type ZnO nano-films were improved by pulsed YAG laser annealing below 532 nm ,and optimum wavelength was 266 nm

(5)Bio-electronics: For sterilization of periodontal bacterium, atmosphere pressure low frequency/temperature micro plasma jet were developed with micro nozzle.

(6)Green technology: The nano/micro bubbles were controlling ejected by laser/focused ion beam fabricated nozzle on piezoelectric vibrator for defecation of water.

Prof. Y. Takano has performed the following studies for iron-based superconductors.

(1) Superconductivity of La Deficient $La_{1-x}OFeP$

(2) Crystal Structure and Superconducting Properties of $Sr_{1-x}R_xFeAsF$ (R=La, Pr, Nd, Sm)

(3) Preparation and Electrical Properties of $SrFeAsF_{1-x}$
(4) Superconducting Properties of $Sr_{1-x}R_xFeAsF_{1-y}$ (R=La, Nd, Sm)
(5) Crystal Structure and Electrical Properties of $LaFe_{1-y}Zn_yAsO$
(6) Preparation and Superconductivity of $LiFe_{1-x}Co_xAs$ and $Li_{1-x}Y_xFeAs$
(7) Electrical Properties of $SrFe_{1-x}Ni_xAsF$
(8) Basic study for the application of $Sr_{1-x}Nd_xFeAsF$ for the superconducting wire rod
(9) Superconducting Properties of $Ca_{1-x}R_xFeAsF_{1-y}$ (R=Nd, Sm)

In study (1), Takano indicated that the origin of the previously reported scattering of T_c in LaFePO was the off-stoichiometry of the samples. In study (2), Takano has firstly prepared $Sr_{1-x}Nd_xFeAsF$ and measured their superconducting properties. Also, in study (8), Takano showed that the upper critical magnetic field of $Sr_{0.5}Nd_{0.5}FeAsF$ was higher than that of MgB_2 that had the highest critical current density. In studies (3) and (4), Takano indicated that the electron doping due to the F deficiency was essentially different from that due to the O deficiency in LaFeAsO and that due to the rare earth substitution in SrFeAsF. Figure 1 shows the relation between T_c and y in $Sr_{0.6}La_{0.4}FeAsF_{1-y}$.

Asso. Prof. T. Asai has has performed the following studies.

(1)Magnetized Coaxial Plasma Gun has been applied for new alloy film deposition technique of Magnetized Coaxial Ion Gun (MCIG) method. This realizes the generation of metallic thin film with the materials which have high-melting-point. Result of the scratch test (JIS R 3255) on an aluminum thin-film formed on a SiO_2 substrate indicates 4.2 times higher adherence strength compared to the conventional vacuum vapor deposition technique. This technique had been applied for a patent via NUBIC. (”Fast alloy film deposition method”, by Tomohiko Asai, Kaoru Suzuki, Nobuyuki Nishimiya, Mikio Takatsu, 2012.9.6 (JP2012-195690)) (Collaboration with Prof. K. Suzuki, Prof. N. Nishimiya and Prof. S. Masutani et al.)

(2)Based on the MCIG, experimental investigations of novel technique of diamond-like Carbon (DLC) generation has been initiated. The functionality of DLC is generally depends on the hydrogen content and ion energy injected into substrate. The MCIG technique potentially controls both hydrogen contents and injection energy of carbon ion. (Collaboration with Mr. M. Hiratsuka and Dr. H. Nakamori et al.)

(3)The application of the LF jet for medical treatments has recently been initiated. In this project, we are focusing on the application to the cancer treatment. The experimental device had been developed (Figure 3) and the initial experiments have been initiated. (Collaboration with Prof. N. Fukuda, Dr. K. Fujiwara, Dr. K. Saito and Dr. H. Koguchi (AIST) et al.)

(4)The muon catalyzed fusion (μCF) is one of the nuclear fusion reaction processes caused in a μ-atom. To improve the efficiency of μCF, innovative concept of fusion reactor design has been proposed and preliminary experiments on a super-Alfvénic translated FRC (Field-Reversed Configuration) plasma have been initiated. (Collaboration with Dr. E. Nakamura (KEK))

Asso. Prof. N. Iwata has has performed the following studies.

(1)The aim of our study is to synthesize the oxides superlattices with atomically sharp interface. The superlattices could be the quite low consumption magnetic devices controlled with electric field, and multifunctional, for example ferroelectric and ferromagnetic multiferroic devices. For the fabrication of the superlattices, highly refined and atomically controllable deposition technique are required. We developed the synthesis of highly dense target, layer-by-layer technique, and carried out the detailed analysis of crystal structures for the superlattices. The materials used were ABO_3 (A=Ca,La,B=Fe,Mn)、$REMO_3$ (RE=La,Bi,M=Fe,$Fe_{1-x}Mn_x$). Although it is difficult to calcine the target with the density more than 95%, the targets of $LaFeO_3$(LFO) : 95.5%、$CaFeO_x$(CFO) : 96.4%、$BiFeO_3$(BFO) : 95.2%、$BiFe_{1-x}Mn_xO_3$(BFMO) : 96.6% were able to be fabricated using the Pechini method by the collaboration research with Prof. Takuya Hashimoto. The superlattices were fabricated by the alternate stacking of the ABO_3 and $REMO_3$ using pulsed laser deposition method.

High quality superlattices grew by a cube-on-cube manner demonstrated by a x-ray diffraction, reflection and reciprocal space mapping, where the superstructure satellite peaks and Laue oscillation were clearly observed. Decreasing temperature, magnetic interaction through the interface was developed expected in the illustration of the temperature and/or magnetic field dependence of in-plain sheet resistance and Hall resistance. In the [CFO/BFMO] superlattice, the saturation magnetization M_S of $0.055\mu_B$ per $Fe_{1-x}Mn_x$ at 300K was observed with the Curie temperature of approximately 450K. The value of the M_S is four times higher than that of bulk BFMO. Novel function can be invested by the synthesis of superlattices.

(2)For the supreme fine FET devices with one nm order in size, the single-walled carbon nanotubes (SWNTs) were synthesized by a chemical vapor deposition (CVD) method with the features of uniform electric property, controlled growth position, and anisotropic alignment. The features are realized by the irradiation of the free electron laser (FEL), surface treatment, and the atomic arrangement of the substrate surface. The alignment growth of the bundled SWNTs were grown on sapphire substrate. The semiconducting SWNTs with four kinds of chirality grew by irradiating the 800nm-FEL. Without the FEL metal and semiconducting mixed SWNTs grew with the chirality more than 30. The reduction of the grown chirality is attributed from the variability of the wavelength and the hundreds femto-seconds micropulses of the FEL. The chirality control during the CVD deposition is successfully carried out at the first time in the world. The synthesis position control and the chirality control were also achieved simultaneously by the surface treatment of a hydrophilic between electrodes.

Assis. Prof. H. Hashiba has has performed the following studies.

(1)One of the promising ways to perform single-photon counting of terahertz radiation consists in sensitive probing of plasma excitation in the electron gas upon photon absorption. We aimed to reveal appearance of plasma excitations under high ratio of incoming photons and at high temperature. Our device is assembled from a GaAs/AlGaAs quantum dot, electron reservoir and superconducting single-electron transistor. The quantum dot is isolated from the surrounding electron reservoir in such a way that when the excited plasma wave decays, an electron could tunnel off the dot to the reservoir. Plasma excitations of the QD arises with a formation of confinement potential barrier from the reservoir having resistances more than resistance quanta, and we revealed that appropriate shape of the barriers lowers dark counts by suppression of flow of hot electrons form the reservoir and reveals higher order excited states. The higher order excited states is expected to have the same plasma frequency of that of the first and shows a heat bath effect of the QD. The detector shows high noise equivalent power of $\sim 10^{-19}$ $WHz^{-1/2}$.

(2)Titanium dioxide (TiO_2) has been draw attention for dye sensitized solar cells by its catalytic characteristics. Our aim is an experimental study of fabrication of fine structures, i.e. photonic crystals, of TiO_2 for solar cells to enhance its efficiency. A TiO_2 thin layer of 150 nm thick was grown on an FTO glass substrate with a fine patterned ZEP resist mask by a conventional RF magnetron sputter method with Ti target. We found that, during the deposition, keeping ratio of Ar-O_2 gas of 2:1 and the deposition ratio of around 0.5 Å/s ensures enough oxygen to form TiO_2 and low temperature to avoid deformation of fine pattern of the ZPU resist mask. Design of the fine patterns is photonic crystal structure of periodic zigzag slabs of 108 nm width, 608 nm in period. TiO_2 layers are white-transparent, amorphous, and those roughnesses are around 7 nm. Baking of TiO_2 fine structures.at 500 ^oC transforms TiO_2 from amorphous to rutile and anatase forms while keeping the same profile of the fine structures. Our new fabrication method can be one of a promising technique to optic devices on researches and industrial area.

Prof. Chaen has performed the following studies. The ensemble of many bio-nanomachines does not represent the real view of the bio-molecule, because the individual reaction does not intrinsically synchronizes with each other. We have studied the biomolecular motor using the ordinary fluorescent

imaging and the receptor protein on the biomembrane using the single-moecule fluorescent imaging technique. Firstly, studies on myosin motor of myosin filament suggested that the movement of myosin molecule was supplied by the thermal fluctuations. Moreover, by developing a new method which can image the chemical reaction occurred the myosin movement, we found that the chemical reaction was influenced by the myosin conformation. Secondly, in the study on the receptor protein of membrane, we have succeeded in improving our microscopy system by selecting a appropriate fluorescent protein, mPlum compared to ordinary fluorescent protein, GFP. And, we have developed a new wet cell using a carbon thin diaphragm to observe a living cell in aqueous solution with scanning microscopy at nanometer resolution.

Asso. Prof. K. Judai has found silver tolylacetylide molecules assembled into a chiral structure, nano helical morphology, even if the acetylide is an achiral molecule. A systematical study of recrystallization solvent revealed that twisted nano helix and non-twisted straight nano ribbon structures can be controlled by the solvents. This may carve out the direction of mirror-symmetry breaking in the homochirality problem.

Appeal achievements

Our group member obtained the following achievements.1). 92 papers; J. Am. Chem. Soc., Nanotechnology and BIOPHYSICS etc., 2) 4 books; Advanced Solid Laser etc., 3) 8 patents; Patent Appl. No.2012-195690 and No.2012-204982, etc., 4) 22 grants; Science, Sports and Culture, a Grant-in-Aid for Scientific Research, etc., 5) 11 awards or articles; “Shiokawa” award, etc.

Conclusions

In this project, the problem of fabricaton of nanomaterials and nanodevices for high functional applications such as electric circuits, biosensor, superconductors, EUV light source, field effect transistor, quantum dot terahertz single photon detector, solid oxide fuel cells, new photo-memory, and bio-nanomotor has been studied. We succeed the following nanomaterials; 1) Superconductivity of La Deficient $La_{1-x}OFeP$ and $Sr_{1-x}R_xFeAsF$ (R=La, Pr, Nd, Sm) etc., 2)Photonic crystals, of TiO_2 for solar cells to enhance its efficiency, 3)Photocatalytic SrxLa1-xTiO3 film for hydrogen generation and p-type ZnO nano-films for light emitting device, 4) Silver tolylacetylide that twisted nano helix and non-twisted straight nano ribbon structures, 5) CeO_2 - ZrO_2 for photo-induced dissociative adsorption of O_2 gas, and nanodevices; 6) Ni or SUS encapsulated carbon nanotube for magnetic force microscope probes, carbon nano-tube/rod and diamond-like carbon diode and chirality controlled single-walled carbon nanotubes for field effect transistor, 7) $LaFeO_3$(LFO)/ $CaFeO_x$(CFO)/ $BiFeO_3$(BFO)/ $BiFe_{1-x}Mn_xO_3$(BFMO) superlattices for ferroelectric and ferromagnetic multiferroic devices, 8) GaAs/AlGaAs quantum dot electron reservoir and superconducting single-electron transistor for single-photon counting of terahertz radiation, 9) Magnetized coaxial plasma gun, Magnetized coaxial ion gun and Low frequency plasma jet, 10) Nano/micro bubbles for water purification, 11) Single-moecule fluorescent imaging for biomolecular motor, myosin motor of myosin filament, Scanning electron microscopy to observe a living cell in aqueous solution.

Quantum theory and computation group

Hiroshi ISHIDA, Shinichiro OHNUKI, Tokuei SAKO,* Tsuneki YAMASAKI

1. Summary of research progress in Quantum theory and computation group

This group aims at understanding the fundamental mechanism and properties of interaction between light and nanomaterial employing quantum/electromagnetic theories and large-scale computation. The highlights of their research achievements are summarized as follows.

2. Electronic properties of solid surfaces and adsorbed molecules (Hiroshi ISHIDA)

Recent progress in microfabrication techniques has enabled us to adsorb molecules at desired positions and to synthesize atomic monolayers in layer-by-layer fashion. Novel quantum phenomena occur in these nano-size systems as a result of energy-level discretization, symmetry lowering, change in the boundary condition of wave functions, and electron correlation effects. In the search for new functional materials and in the development of nano-size devices, the importance of theoretical calculations are ever increasing as a tool to analyze and predict experimental observations. In the present work, we conducted theoretical calculations of the electronic structure of solid surfaces and adsorbed molecules by placing emphasis on "the effects of strong electron correlations" and "the calculation of truly semi-infinite solid surfaces".

(2-1) Electronic structure of the Metal/Mott insulator interfaces

An important question from a view point of device application is whether a device such as tunnel junctions works properly when a band insulator is replaced by a Mott insulator originating from strong electron correlations. As a theoretical technique to treat strongly correlated systems, dynamical mean-field theory (DMFT) is widely used. In particular, for bulk crystals, its extension to cluster type DMFT methods where electron correlations among neighboring atomic sites are taken into consideration are becoming standard. On the contrary, DMFT calculations for surface systems were so far restricted to those using the single-site approximation. In the present work, we applied the cluster DMFT technique to correlated surface and interface systems. It was demonstrated that the mechanism of the metal-to-insulator transition in the correlated layers as well as the tunneling conductance through them changes qualitatively from those obtained by the single site DMFT. Similarly, we calculated the electronic structure of a monolayer of the Mott insulator adsorbed on a semi-infinite non-interacting metal substrate. While in the single DMFT, the overlayer becomes a Fermi liquid due to proximity effects to the metal substrate, it was found that the overlayer remains a non-Fermi liquid in the cluster DMFT calculation to much lower temperatures.

(2-2) Coulomb blockade and Kondo effect in the Hubbard molecule

It has become possible to measure conductance of single molecules connected to metal electrodes. On the theory side, calculations of the ballistic conductance for molecules are reported based on the Landauer formula and density functional theory (DFT). The agreement between theory and experiment is not necessarily good as DFT cannot treat many body effects caused by strong Coulomb interactions between electrons in the molecules. To address this issue, we considered a N-site Hubbard molecule bridging two non-interacting semi-infinite metallic electrodes and calculated its electronic structure in the limit of the zero bias voltage by using the exact diagonalization technique. It was shown that our method can describe Coulomb blockade effects as well as the formation of Kondo resonance at low temperature originating from the coupling of localized spins in the molecule and conduction electrons in the electrodes.

(2-3) Rashba effects in the localized surface bands of crystal surfaces

Spin-orbit interactions play an important role in the electronic structure of crystal surfaces. One example is the topologically protected surface states of topological insulators. Another is the spin

polarization of localized surface bands observed in nonmagnetic materials such as Ag and Bi. The latter is called the Rashba effect. Previous first-principle calculations of the Rashba effect within DFT were performed by approximating crystal surfaces by thin slabs. However, the slab model is not suitable for the accurate description of localized surface states and surface resonances, since the bulk energy levels in the normal direction are discretized. We have incorporated the spin-orbit interaction term in our embedded Green's function program and performed first-principles DFT calculations of the Rashba effect for a number of truly semi-infinite surfaces. As an example, we show in Fig. 1 the calculated surface band structure of Bi/Ag(111) surface, where we plotted the intensity map of $\rho(\varepsilon, \boldsymbol{k})$, the k-resolved local density of states within a muffin-tin sphere of an outermost surface atom, as functions of the wave vector and one-electron energy. The dark regions correspond to the energy gaps of projected bulk energy bands. Bright lines in the energy gaps are the localized surface states. As the Kramers degeneracy is lifted at the surface due the lack of the space inversion symmetry, the surface bands become spin-polarized except for the the Γ point in surface Brillouin zone.

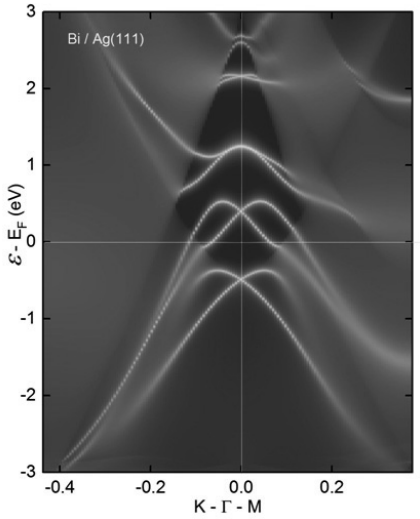


Fig.1 Bi/Au(111)表面の Rashba 効果

3. Nano-Electromagnetic Simulation for Light-Material Interactions (Shinichiro OHNUKI)

We have developed fast and reliable electromagnetic simulation methods for studying interaction between light and nanoscale objects. We apply our novel methods to designing nanoscale devices for high-speed and high-density magnetic recording, quantum telecommunication, and so on. This research was awarded the 2013 academic award from College of Science & Technology, Nihon University and the 2013 best paper of Magnetics Society Japan.

(3-1) Time Domain Responses of Electromagnetic Fields by Integral Equation Methods

We have developed novel fast and accurate solvers based on integral equation methods with fast inverse Laplace transform for time domain electromagnetic problems. The advantages of our proposed method are (1) the computational error is easy to be controlled, (2) there is the no restriction of selecting time step size, and (3) an arbitrary observation time can be selected. Using the combination of fast algorithms and parallel computing, the speedup rate becomes over 100 times faster. We have designed plasmonic antennas which can localize circularly polarized light in nanoscale.

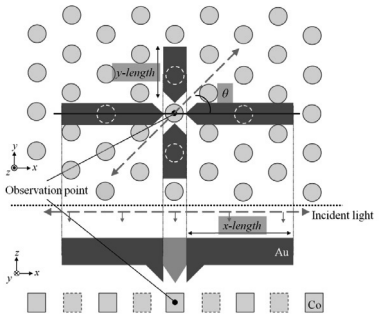


Fig.2 Proposed system for high-density all-optical magnetic recording.

(3-2) Design of Plasmonic Antennas with Bit-Patterned Media for High-Density Magnetic Recording

We study characteristics of plasmonic antennas with bit-patterned media to realize high-density all-optical magnetic recording through the collaboration with Prof. Katsuji Nakagawa, Information Group. Figure 2 shows an asymmetric cross antenna constituted by two dipole antennas with bit-patterned media. Antenna lengths are selected to obtain 90° phase shift. Localized circularly polarized light is generated inside the particulate medium at the center of antennas. In our proposed system, the

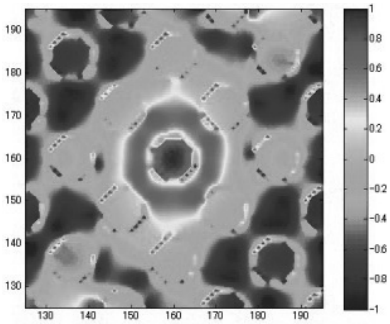


Fig.3 Circularity inside the bit-patterned media.

recording density can be achieved over 2Tbit/inch^2. We investigate the motion and required DC field of magnetization reversal using micro magnetics simulation in collaboration with Prof. Arata Tsukamoto, Information Group, as in Fig.3.

(3-3) Multiphysics Simulation of Nanoscale Objects in Laser Fields

We have developed the coupled Maxwell-Schrödinger scheme which is based upon the FDTD method in collaboration with Prof. Tokuei Sako, Quantum Theory and Computation Group. Our proposed method can handle tunneling effects due to well structures. We have investigated current densities and electromagnetic fields of nano plates. Advantages of our method have clarified in comparison with conventional classical solvers (Fig. 4). We have investigated the interaction between the light control pulse and thin tube including only a single electron, where the pulse is designed to control the electron-state. Our designed pulse has excellent ability to control the electron state with high accuracy (Figs. 5 and 6).

(3-4) Modeling of Plasmonic Waveguides for a High Sensitivity Optical Sensor

We have proposed an optical sensor which consists of a metal stripe and nano wire. Using the proposed device, electromagnetic energy is concentrated around the metal stripe and the energy can be efficiently absorbed into the nano wire. Joule heat inside the nano wire is produced due to the electromagnetic energy and becomes over 50 times higher than that for the case without the metal stripe.

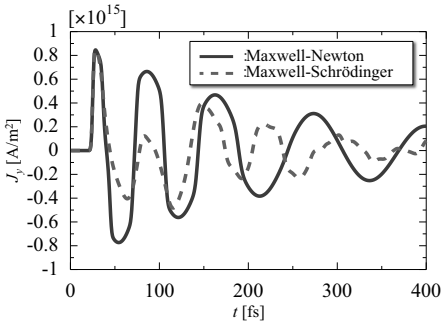


Fig.4 Time domain response of current density in a nano plate.

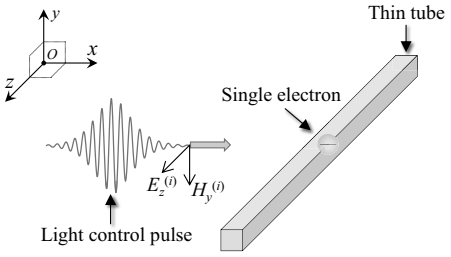


Fig. 5 Nano tube and the coordinates.

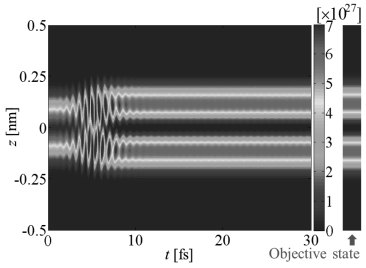


Fig. 6 Control of electrons states by a

4. Origin of Hund's rule and angular correlation in natural and artificial atoms (Tokuei SAKO)

Artificial atoms or quantum dots, novel quantum systems confining a small number of electrons in a low-dimensional artificially-designed nanoscale potential well, play an essential role in the development of next generation devices operating under the principle of quantum mechanics, utilized in, such as, quantum computation and quantum telecommunication. Since the electronic properties of artificial atoms are known to depend strongly on their size and/or number of electrons, understanding their complicated electronic structure is one of the most fundamental and essential issues. In this direction the author has focused on in this *N.* project the origin of so-called Hund's rule and studied the mechanism of this fundamental rule operating in artificial atoms. An inherent hole in the spin-parallel singlet wave function has been identified and is called *conjugate Fermi hole*. It has been shown that the origin of Hund's rule is rationalized on the basis of this conjugate-Fermi-hole concept.

(4-1) Origin of Hund's multiplicity rule

Empirically derived Hund's rules of pre-quantum-mechanics era that predict the ordering of the energy levels possessing different spin and orbital angular momentum quantum numbers proved to be almost universally valid for atoms, molecules, and quantum dots. Yet, despite the history of a long standing debate the search for various aspects of their origin persists, that was most likely due to our lack of knowledge as to how electrons in the system behave differently for different spin states. We explore the origin of the first Hund rule for a two-dimensional model of He-like systems and that of two-electron quantum dots which represent ideal systems providing a direct fundamental insight into the structure of the internal part of the fully-correlated wave functions, allowing us an unambiguous

argument. An examination of their probability density distributions indeed reveals the existence of a region in the internal space which we refer to as a conjugate Fermi hole (Fig.7 Phys. Rev. A 2011). In this region the singlet wave function has a smaller probability density than the corresponding triplet one, in contrast to a genuine Fermi hole in which case the triplet has a smaller density than the singlet. Thanks to the presence of this conjugate Fermi hole, the singlet probability density has to migrate far away from the center of the one-electron potential, rationalizing thus a well-known broader electron density distribution of the singlet state than is the case for the corresponding triplet, that is a key observation to explain the singlet-triplet energy gap. This result was published in Journal of Physics B in 2012 and was chosen as IOP Select Paper, which was further covered by Europhysics News published by the European Physical Society. He was invited by JPS to write a review article on this subject in BUTSURI, that was published recently in the June issue of 2013 with the title "Origin of the First Hund Rule in He-Like Atoms".

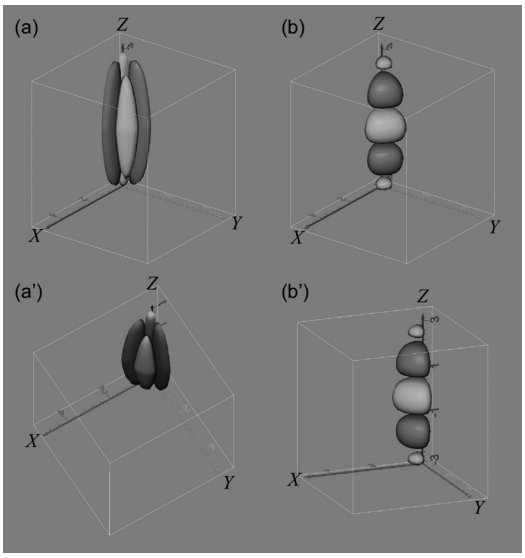


Fig.7 Structure of standard Fermi holes (blue) and *conjugate Fermi holes* (red) in the internal space of two electron.

5. Switching Effect and Confinement efficiency by Dielectric Waveguide with Photonic Nanostructures (Tsuneki YAMASAKI)

We have analyzed the scattering and guiding problems by dielectric waveguides with defects composed of dielectric circular cylinders array loaded with dielectric rectangular cylinder and arbitrary dielectric structure in the middle layer, and investigated the influence of power transmitted coefficients by using the combination of improved Fourier series expansion method and multilayer method and the distribution of energy flow for defect area utilizing the propagation constants at the guided region. We have investigated the optimum dielectric structure to obtain the switching effects or confinement efficiency. Numerical results are given for the influence of the incident angle and normalized frequency of the transmitted power in terms of the parameter $\varepsilon_3/\varepsilon_0$ of the rectangular cylinders in the middle layer sandwiched between two multilayers, yielding the basis characteristics of resonance peak for switching or frequency selective devices for both TM and TE cases.

(5-1) Confinement efficiency of photonic structure for case of loaded with arbitrary dielectric structures

We consider the dielectric waveguides composed of dielectric circular cylinder array with air-hole type circular cylinder array. Figure 8 shows the distribution of energy flow at the guided area for types A and B as condition of excited normalized frequency $p/\lambda = 0.4814$ and $p/\lambda = 0.4368$, respectively. And also, the circles of solid and dashed lines denote the position that it is placed the dielectric circular cylinders or air-hole circular cylinders. Form these results, we can see the following features: (1) From a comparison of structure type A and type B, the energy of defect area for type B can be concentrated than that of structure type A. (2) We obtained the confinement efficiency by type B compared with previous structure type A.

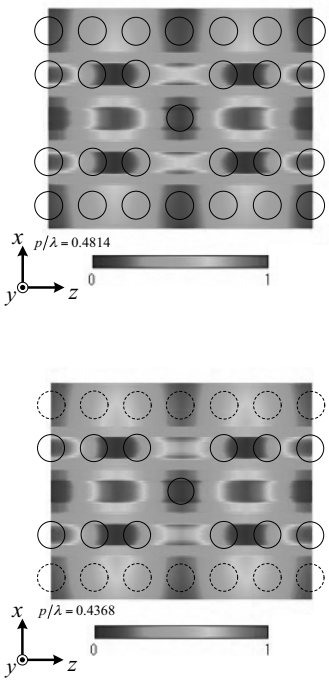


Fig.8 Distribution of energy flow at guided area for types A (upper) and B (lower).