PCSI

Room Ballroom South - Session PCSI-MoA

Magnetism/Spintronics I/Organics/Nanostructures

Moderators: Martin Brandt, Walter Schottky Institut, Technische Universität München, Paul M. Koenraad, Eindhoven University of Technology, Netherlands, Daniel Loss, University of Basel, Giovanni Vignale, University of Missouri-Columbia

2:00pm **PCSI-MoA-1 Magnetic Dipole-dipole Sensing at Atomic Scale using Electron Spin Resonance STM***, **Taeyoung Choi**, W Paul,* IBM Almaden Research Center*; S Rolf-Pissarczyk,* Max Planck Institute for the Structure and Dynamics of Matter, Germany*; A Macdonald,* University of British Columbia, Canada*; K Yang,* IBM Almaden Research Center*; F Natterer,* École Polytechnique Fédérale de Lausanne, Switzerland*; C Lutz,* IBM Almaden Research Center*; A Heinrich,* Ewha Woman University, Republic of Korea **INVITED**

Magnetometry having both high magnetic field sensitivity (energy resolution) and nanoscale spatial resolution has been of great interest and an important goal for applications in diverse fields covering physics, chemistry, material science, and biomedical science. The scanning tunneling microscope (STM) has been one of the most versatile tools for atomic-scale imaging, manipulation, and tunneling spectroscopy.

Here, we successfully combine electron spin resonance (ESR) and STM, coherently driving spin resonance of individual iron (Fe) atoms on surfaces (MgO/Ag(100)) [1]. A radio-frequency electric field (~20 GHz), applied at the tunneling junction, modulates the spin state of the Fe atoms. The spin resonance signal is detected by a spin-polarized tunneling current. The ESR signals from individual Fe atoms differ by a few GHz (~10 μeV) while the ESR linewidth is in the range of only a few MHz (~10 neV). Such a high energy resolution enables us to distinguish spin distributions down to single-atom level and to investigate weak magnetic interactions.

When we placed two Fe atoms close together with controlled atom manipulation, we found that the ESR signal from each Fe atom splits into doublet, of which separation depends on the distance between two atoms. Our measurements show $r^{-3.01\pm0.04}$ distance-dependent splitting, in excellent agreement of magnetic dipole-dipole interaction. We utilized this precisely measured dipolar interaction to determine the location and magnetic moment of unknown spin centers with sub-nanometer and one hundredth of Bohr magneton precision [2].

Our ESR-STM may promise the STM as a new and unique platform for a quantum sensor, investigating spin-labeled molecular structures and a quantum information processor, modeling quantum magnetism. We gratefully acknowledge financial support from the IBM and Office of Naval Research.

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2:30pm **PCSI-MoA-7 Mechanism of Stabilization and Magnetization of Impurity-doped Zigzag Graphene Nanoribbons***, Y Uchida, S Gomi, H Matsuyama, A Akaishi,* ***Jun Nakamura**,* The University of Electro-Communications (UEC-Tokyo), Japan

In recent years, a considerable number of studies have focused on the modification of the electronic structure of graphene by nitrogen or boron doping. It has been reported that N atoms prefer to locate near the so-called zigzag edge of graphene, but it is not always understood why this should be so. In addition, every study has suggested a different interpretation of the appearance of impurity levels of dopants located near the zigzag edge of graphene nanoribbons (GNRs). Here, we propose the charge transfer model that satisfactorily explains the structural stability and the electronic structure of the impurity-doped zigzag GNR (ZGNR).

The structural stability and the electronic structure of doped ZGNR have been investigated using first-principles calculations based on the density functional theory. The formation energy of doping increases as a function of the distance between the N (B) atom and the zigzag edge, and two tendencies are observed depending on whether the dopant is an odd or even number of sites away from the zigzag edge. Such an energetic dependence is successfully explained by the charge transfer model; when the N (B) atom dopant is located near the edge, the extra electron (hole) of the N (B) atom transfers to the edge state, resulting in the occupation (vacation) of the originally-unoccupied (occupied) edge state. Since the edge state has amplitude only at odd-numbered sites, only the N-2p_z orbital at odd-numbered sites can resonate with the edge state; thus, the eigenvalue of the edge state for odd-numbered-site doping becomes lower than that for even-numbered-site doping. The gain in the electrostatic energy between the N cation (B anion) and the extra electron (hole) delocalized at the edge decreases with increasing distance of the N (B) atom from the edge, which leads to the trend of increasing formation energy. On the other hand, when the N (B) atom dopant is located sufficiently away from the edge, the extra electron (hole) is no longer transferred to the edge, but occupies the π*-band (π-band), which results in a kinetic energy gain because of the large energy dispersion of the π*-band (π-band) [1].

Such an electron (hole) transfer leads to the compensation (disappearance) of the local spin-magnetic moment at one side of the ZGNR, manifesting in the ferromagnetic ground state of ZGNR. Our findings will open up a route for development of new types of lightweight magnetic materials.

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2:35pm **PCSI-MoA-8 Magnetoresistance and Electrically Detected Magnetic Resonance Study of Leakage Currents in Low-k Dielectrics***, **Ryan Waskiewicz**, M Mutch, P Lenahan,* Penn State University*; S King,* Intel Corporation

Leakage currents in low dielectric constant thin films utilized in present day integrated circuitry are important reliability concerns. We have initiated a study of the defects involved in electron transport through low-*k* films utilizing both electrically detected magnetic resonance (EDMR) and low field magnetoresistance (MR) measurements. The EDMR and MR response involves spin dependent trap assisted tunneling [1]. The investigated sample structures were p-Si/a-SiOC:H/Ti. In the MR measurement, we observe a response very similar to the EDMR response at resonance, but the MR response occurs around zero magnetic field applied and is due to a mixing of singlet and triplet defect electron states. We investigate the gamma radiation response of leakage currents in dense and porous a-SiOC:H thin films, which are utilized in industry. (The changes generated are likely also relevant to high electric field behavior in these films.)Representative EDMR and MR spectra for the porous films as a function of bias during irradiation are illustrated in Fig. 1. Before gamma irradiation, we observe a weak MR response and nearly no EDMR response. Along with changes in leakage currents after 15 Mrad irradiation, we observe a large increase in both MR and EDMR response although the MR response remains larger than then EDMR response. A qualitatively similar response is observed in the dense films (not shown). The response of these films as a function of applied bias has also been studied with both EDMR and MR measurements. The amplitude of both the EDMR and MR responses increase linearly with applied Ti gate bias. At a negative bias, both responses are below detection limits. This bias response allows us to draw some conclusions about defect energy levels, which will be provided during the conference. This bias response also suggests that the defects responsible for the EDMR and MR are the same defect. As a continuation of this study, we will further study the response of these films with stressing and attempt to identify the defect(s) responsible for transport, now tentatively identified as Si dangling bonds before irradiation and C dangling bonds after irradiation [2]. This project is sponsored in part by the Department of Defense, Defense Threat Reduction Agency under grant number HDTRA1-16-0008. The content of the information does not necessarily reflect the position or the policy of the federal government, and no official endorsement should be inferred.

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[1] M. Mutch, P. Lenahan, and S.King, *J. Appl. Phys.* **119**, 094102 (2016).

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2:40pm **PCSI-MoA-9 Interface Characterization via Spin Dependent Charge Pumping***, **Mark Anders**, P Lenahan,* Penn State University*; A Lelis,* U. S. Army Laboratory

Electrically detected magnetic resonance (EDMR) has been very useful in the study of point defects in semiconductor/insulator heterojunctions. Nearly all of these EDMR interface studies have utilized spin dependent recombination (SDR). Although SDR EDMR is quite sensitive (>10^7 times the sensitivity of EPR). It utilizes a recombination current, so it is only highly sensitive to deep level defects. We show that a new EDMR technique, spin dependent charge pumping (SDCP) [1], overcomes this limitation, allowing EDMR measurements of defects with levels in most of the band gap. SDCP is also significantly more sensitive than SDR based interface methods. In

SDCP, a trapezoidal waveform is applied to the gate which cycles the Fermi level from near the conduction to valence band edges. Interface traps are filled, then emptied which creates a current that allows measurement of defects throughout most of the band gap. Like SDR EDMR, we find the sensitivity of SDCP is very nearly field and frequency independent, allowing for a wide range of resonance frequency and field SDCP measurements from 5600 Gauss to 35 Gauss. In addition, we find that there is a strong SDCP response near zero magnetic field. We believe this response involves physics similar to the low field magnetoresistance observed in organic semiconductors. SDCP at low resonance field and frequencies allows for: (1) partial separation of spin-orbit coupling and hyperfine effects on magnetic resonance spectra, (2) observation of otherwise forbidden half-field effects [2] which make EDMR, at least in principle, quantitative, and (3) observation of Breit-Rabi shifts [3] in superhyperfine measurements. We present results on 4H-SiC nMOSFETs, but the approach utilized should be widely applicable to other heterointerfaces such as Si/SiO_2, Si/High-K, and SiGe/insulator systems. Although the abstract length is too short to discuss all results, we illustrate a representative ultra-low resonance frequency (85 MHz) SDCP spectrum in Fig.1. Fig 1(a) illustrates the Breit-Rabi shift of the 10.4 Gauss doublet, a hydrogen complexed E' center spectrum. Fig. 1(b) illustrates the half-field resonance response due to the "forbidden" transitions created by magnetic dipole-dipole moment interaction between defects. Its intensity, in principle, allows a precise quantitative measurement of the defect density via EDMR [4]. The strong response near zero magnetic field can provide some hyperfine information and EDMR-like detection in fully processed devices without the expense and complexity of a resonance spectrometer.

2:45pm **PCSI-MoA-10 Theory of the Nonlocal Anomalous Hall Effect***,* ***Giovanni Vignale****, S Zhang,* University of Missouri-Columbia **INVITED**

The anomalous Hall effect is deemed to be a unique transport property of ferromagnetic metals, caused by the concerted action of spin polarization and spin-orbit coupling. Nevertheless, recent experiments have shown that the effect also occurs in a nonmagnetic metal (Pt) in contact with a magnetic insulator [yttrium iron garnet (YIG)], even when precautions are taken to ensure that there is no induced magnetization in the metal. We propose a theory of this effect based on the combined action of spin-dependent scattering from the magnetic interface and the spin-Hall effect in the bulk of the metal. At variance with previous theories, we predict the effect to be of first order in the spin-orbit coupling, just as the conventional anomalous Hall effect - the only difference being the spatial separation of the spin-orbit interaction and the magnetization. For this reason we name this effect "nonlocal anomalous Hall effect", and we predict that its sign will be determined by the sign of the spin-Hall angle in the metal. The anomalous Hall conductivity that we calculate from our theory is in order of the magnitude agreement with the measured values in Pt/YIG structures.

3:15pm **PCSI-MoA-16 Spin-Polarized Current Injection Induced Magnetic Reconstruction at Oxide Interface***,* ***Gunter Luepke****,* College of William & Mary

Electrical manipulation of magnetism presents a promising way towards using the spin degree of freedom in very fast, low-power electronic devices. Though there has been tremendous progress in electrical control of magnetic properties using ferromagnetic (FM) nanostructures, an opportunity of manipulating antiferromagnetic (AFM) states should offer another route for creating a broad range of new enabling technologies. Here we selectively probe the interface magnetization of $SrTiO_3/La_{0.5}Ca_{0.5}MnO_3/La_{0.7}Sr_{0.3}MnO_3$ heterojunctions and discover a new spin-polarized current injection induced interface magnetoelectric (ME) effect [1]. The accumulation of majority spins at the interface causes a sudden, reversible transition of the spin alignment of interfacial Mn ions from AFM to FM exchange-coupled, while the injection of minority electron spins alters the interface magnetization from C-type to A-type AFM state. In contrast, the bulk magnetization remains unchanged (Fig. 1). We attribute the current-induced interface ME effect to modulations of the strong double-exchange interaction between conducting electron spins and local magnetic moments. The effect is robust and may serve as a viable route for electronic and spintronic applications.

4:30pm **PCSI-MoA-31 Organics Invited 2***,* ***Markus Wohlgenannt****,* University of Iowa **INVITED**

5:00pm **PCSI-MoA-37 Microwave Magnetization Dynamics in Room Temperature Organic-Based Magnets: From Fundamental Studies to Emerging Applications***,* ***Ezekiel Johnston-Halperin****, M Chilcote, A Franson, M Harberts, Y Lu, H Yu,* The Ohio State University*; N Zhu,* Yale University*; I Froning,* The Ohio State University*; X Zhang,* Yale University*; R Adur, C Hammel, A Epstein,* The Ohio State University*; M Flatte,* University of Iowa*; H Tang,* Yale University

Organic and organic-based materials are attractive candidates for applications in magnetoelectronics and spintronics due to their low cost, ease of fabrication, and low spin-orbit coupling (and consequently long spin lifetimes). More recently, advances in these fields have highlighted the potential for dynamic excitations to drive new phenomena such as ferromagnetic resonance generated spin-pumping. Here we present a series of recent breakthroughs in the synthesis, encapsulation, and measurement of organic-based magnets that lay the foundation for all organic magnetoelectronic and spintronic devices. We will discuss advances in encapsulation strategies that allow lifetimes of up to 1 month in air [1], the use of ligand substitution to generate a library of related magnetic materials [2], the growth of all-organic and hybrid organic/inorganic magnetic heterostructures, and measurements of ferromagnetic resonance (FMR) linewidths of ~ 1 Oe [3], comparable to yttrium iron garnet (YIG). Finally, we demonstrate the potential for real world applications in the construction of a V[TCNE]2 based spin-wave resonance device with spectral tuning from 1 – 5 GHz and a quality factor in excess of 3,200 that operates under ambient conditions [4]. These results establish the validity of organic-based magnets for applications in next-generation magnetoelectronics and provide unique leverage on long-standing challenges in the field of organic spintronics.

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5:05pm **PCSI-MoA-38 Characterization of Energy Conversion Behavior in Nanostructured PEDOT Polymer-Graphene Composite***, M Sakr, S Abdel-Nasser,* ***Mohamed Serry****,* American University in Cairo, Egypt

One of the major drawbacks for successful application of graphene in energy storage and conversion applications is its cone shaped band gap. Therefore, several ongoing researches are currently focusing on the opening of the graphene band gap by doping, patterning and applying electric field on graphene layers [1]. Accordingly, in this work, we study a new composite structure consisting of nanostructured conducting polymer deposited on the surface of graphene-Schottky-diode (Conducting-Polymer/Graphene/Pt/n-Si) for enhanced energy storage and opto-electrical energy conversion applications. Poly (3,4-ethylenedioxythiophene) (PEDOT) was selected as the organic semiconductor material because of its low band gap (1.5−1.7 eV), long-term stability as well as good electrical conductivity. Significant enhancement in the dark current from 99 µA for the bare graphene-Schottky devices to 20 mA for the PEDOT composite structures at −10V bias which corresponds to more than 196 times enhancement in current. The morphology of the composite electrodes (Fig. 1) shows very well dispersed particles of the deposited polymers on the graphene surface. Fig. 2 (a) shows the dark I-V characteristics of the composite electrodes as well as the bare material, which illustrates a distinctive increase in the current behavior for all the PEDOT composite samples with respect to the bare graphene samples. The current response was extensively increased upon the deposition of PEDOT reaching 4.7 mA for the 200 µl PEDOT volume.

5:10pm **PCSI-MoA-39 Applications of Switchable Interfacial Dopants***,* ***Peter Kruse****, A Mohtasebi, T Chowdhury, E Hoque, O Sharif,* McMaster University, Canada

Doping of bulk semiconductors and low-dimensional structures (carbon nanotubes, graphene, etc.) in order to modulate their electronic properties is a well-established concept.[1] However, it is usually permanent. Even in cases where doping of thin films by analytes (e.g. carbon nanotubes by ammonia) is applied in sensors, it is only reversed by physical removal of the dopant molecules, e.g. through heating. On the other hand, molecular switches are also an old concept by now, but practical examples of facile detection of their state with a thin film sensor are less common. We demonstrate the facile doping and de-doping of iron oxide films as well as carbon nanotube networks in contact with different oligoaniline oxidation states as an example of interfacial doping with a switchable dopant, i.e. a molecular switch. The idea that a small local change in carrier concentration (in this case due to a modification of the doping state) results in a large change in resistivity is somewhat reminiscent of (but not identical to) a chemical field effect transistor (in which case the electric field is modulated due to creation of electric charges), in that it also constitutes an active sensor. While for most conventional sensing applications, the removal of the dopants from the film present one challenge and the selectivity to a particular dopant another, even bigger, challenge, our devices keep the dopants in place. The sensing performance is achieved by switching the dopants between active and inactive states. A redox sensor for measuring chlorine concentrations in drinking water [2] is the first member of this new class of sensors, although the concept certainly can be applied to many other systems. Not only are these systems relevant for sensors, but charge transfer in closely coupled redox systems (e.g. oligonanilines and iron oxide) also find applications in corrosion inhibition [3] and smart coatings, another application that we are exploring in our group.

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5:15pm **PCSI-MoA-40 On the Possibility of the Development of Vicinal Superlattices in Quantum Wires on Semiconductor Low - Index Surfaces***, **Victor Petrov,*** Russian Academy of Science, Russian Federation

As is well known, vicinal superlattices (VSLs) are realized in 2D electron systems on semiconductor high-index Miller surfaces. The possibility of existence of such VSLs was predicted theoretically [1,2]; simultaneously and independently they were realized [3]. The existence of SL effects in VSLs is due to the appearance in these systems of a new cristallographic translation period in the plane of quantum wells A >> a_0 (a_0 is the lattice constant). A new translation period A produces minigaps (MGs) in the energetic spectrum of the particles in these systems and, as a result, different SL effects. At the present time, all these VSLs are developed only in 2D systems. At the same time, it is known that superlattice effects should be maximal in quantum wires (QWR) when the SL period A appears along the axis of the QWR.

In this work we suggest a new method of development of VSL in QWR on semiconductor low-index surfaces. For this purpose we suggest to orient the axis of the QWR at the necessary angles to the basic translation vectors on a low-index surface. In this case in the QWR the new basic translation period along the axis of the QWR A > > a_0. Thus, the period A along the surface in the one-dimensional VSL is selected by the orientation of the QWR on the low-index surface. If the QWR is realized in the MOS system with the use of a narrow gate [4] then the orientation of the wire will be determined simply by the appropriate orientation of the gate. The analytic expressions of the new periods A were obtained as a function of the angles which determine orientation of the QWR for the different low-index surfaces GaAs and Si. The positions of MGs in the one-dimensional k-space were determined. It is should be noted that in the region of the particle wave function localization in the QWR there are many crystallographic planes which form a SL energetic spectrum of the particle. Illustrative estimates of the magnitude of the MGs for the QWR of the rectangular cross-section made in the weak coupling approximation demonstrate their dependence on the geometric parameters of the cross-section, on the period A as well as on the crystal potential.

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5:20pm **PCSI-MoA-41 Site-dependent Oxygen Reduction Reaction of N-doped Graphene Nanoclusters***, **Haruyuki Matsuyama,** S Gomi, M Ushirozako, A Akaishi, J Nakamura,* The University of Electro-Communications (UEC-Tokyo), Japan

Nitrogen-doped graphene exhibits high oxygen reduction reaction (ORR) activity [1]. Recently, it has been theoretically revealed that nitrogen atoms prefer to locate near the zigzag edge of graphene [2]. Therefore, many theoretical researchers have focused on the nitrogen atom existing at the graphene edge. In this study, we focus on the role of edge structures of nitrogen-doped graphene on the ORR activity.

We investigated the ORR activity for the hexagonal nitrogen-doped graphene nanoclusters having zigzag or armchair edges, using first-principles calculations within the density functional theory. Electrocatalytic activities were evaluated on the basis of the computational hydrogen electrode model proposed by Nørskov *et al.* [3] In general, the ORR mainly proceeds in two pathways: For the two-electron pathway ($2e^-$), O_2 is reduced to hydrogen peroxide (H_2O_2), and for the direct four-electron pathway ($4e^-$), the final product is water (H_2O). H_2O_2 for the $2e^-$ pathway might erode electrocatalyst materials, leading to low durability. Therefore, we also pay attention to the selectivity for the $4e^-$ pathway.

Figure 1 shows a model of the zigzag graphene nanocluster. Doping sites of nitrogen atoms are indicated in this figure. Figure 2 shows maximum electrode potentials for ORR at each doping site. The maximum potential for the $4e^-$ pathway is higher than that for the $2e^-$ pathway in almost all reaction sites. It is noted that the high selectivity for the $4e^-$ pathway is assured not just at the edge but inside the cluster. The effects of edge structures, cluster sizes, and doping configurations on the ORR activity will be discussed in the presentation.

5:25pm **PCSI-MoA-42 Nanopore Formation with Au Cluster via Ostwald Ripening for Optical Nanobio Sensor***, **SeongSoo Choi,** M Park, C Han, S Oh,* SunMoon University, Republic of Korea*; D Park,* Hallym University, South Korea*; Y Kim,* Sungkyunkwan University, Republic of Korea*; N Park,* Seoul National University, Republic of Korea

There have been tremendous interests about the fabrication of portable optical nano-biosensor due to its potential application of single molecule analysis such as DNA and RNA, and protein. Recently the fabrication of the portable device with an electrical detection technique (MinION by Oxford nanopore technology) was reported, however, the high error rate for DNA analysis were reported and are being hindered its practical application [1]. In this report, we will address the fabrication of optical nanopore by using plasmonic effect. The freestanding ~ 40 nm thick Au films were obtained by using conventional sputter deposition of Au on the SiN films followed by removal of supporting SiN film with a plasma etching technique. The deposited Au films would consist of the mixture of various size Au nanoclusters and nanoparticles. Depending upon the Au cluster size, the melting points would vary due to the cluster shell model. The ~ 100 nm diameter Au aperture was initially fabricated with 30 keV Ga ion focused ion beam on the deposited Au film. Then, the Au pore membrane incorporated with carbon atoms inside the 100 nm diameter Au aperture was formed under electron beam irradiations The Au pore-membrane incorporated with carbon atoms under electron beam irradiations were formed. Initially, the Au atoms (less than 1 nm) on the diffused pore membrane were not able to be detected due to resolution limit of TEM. ~ 1 nm. When the samples were kept under the room environment for several months, the Au nanoclusters were formed on the diffused membrane [2]. During electron beam irradiations, melting of the Au films would be dependent upon the Au nanocluster size, conductivity of the Au films, electrical contacts between the specimen and the sample holder, etc. Under the laboratory environments, the Au clusters on the diffused membrane were formed via Ostwald ripening [2]. The spinodal decoposition, i.e, unstable structural change of the Au structures in the amorphous Au-C membrane system [3] were observed during electron beam irradiations. The Au clusters formed on the Au-C pore membrane can be utilized as an optical nanopore sensor.

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5:30pm **PCSI-MoA-43 Tunable-Composition Multi-Component Thin Films using Split-Target Pulsed Laser Deposition***, **Wayne McGinnis**, A Hening, T Emery-Adleman,* SPAWAR Systems Center Pacific

A new technique has been developed that uses pulsed laser deposition (PLD) with a two-part (split) ablation target to grow thin layers of a multi-component oxide film with improved control over the resultant film elemental composition. One often heralded advantage of PLD for growth of chemically complex materials is stoichiometric transfer of the target material to the substrate. In some cases, though, target stoichiometry is preserved only under very specific deposition conditions that vary depending on the target material and the substrate temperature. Such conditions are often difficult and time-consuming to determine. The new technique overcomes these difficulties, and has been used to demonstrate the ability to grow mixed-metal oxide films of varied stoichiometry from a single split target.

5:35pm **PCSI-MoA-44 Effective Nitrogen Doping into TiO_2 for Visible Light Response Photocatalysis by Ion Implantation Technique***, **Tomoko Yoshida**,* Osaka City University, Japan*; S Niimi, M Yamamoto, S Yagi,* Nagoya University, Japan

Photocatalytic reactions at the surface of titanium dioxide (TiO_2) under UV light irradiation have been attracting much attention in view of their practical applications to environmental cleaning such as self cleaning of tiles, glasses, and windows. Recently, Asahi *et al.* reported that the doping of nitrogen into TiO_2 contributes to band gap narrowing to provide visible-light response.

In the present study, the thickness-controlled TiO_2 thin films were fabricated by thepulsed laser deposition (PLD) method. These samples functioned as photocatalysts under UV light irradiation and the reaction rate depended on the TiO_2 thickness, i.e., with an increase of thickness, it increased to the maximum, followed by decreasing to be constant. Such variation of the reaction rate was fundamentally explained by the competitive production and annihilation processes of photogenerated electrons and holes in TiO_2 films, and the optimum TiO_2 thickness was estimated to be ca. 10 nm

We also tried to dope nitrogen into the effective depth region (ca. 10 nm) of TiO_2 by an ion implantation technique. The nitrogen doped TiO_2 enhanced photocatalytic activity under visible-light irradiation. XANES and XPS analyses indicated two types of chemical state of nitrogen, one photo-catalytically active N substituting the O sites and the other inactive NOx ($1 \le x \le 2$) species (Fig.1). In the valence band XPS spectrum of the high active sample, the additional electronic states were observed just above the valence band edge of a TiO_2. The electronic state would be originated from the substituting nitrogen and be responsible for the band gap narrowing, i.e., visible light response of TiO_2 photocatalysts.

5:40pm **PCSI-MoA-45 Study on Photodeposition Process of Pt Nanoparticles on TiO_2 Photocatalyst by XAFS Spectroscopy***, **Yuji Nakano**, M Akatsuka, M Yamamoto, C Tsukada, S Ogawa, S Yagi,* Nagoya University, Japan*; T Yoshida,* Osaka City University, Japan

TiO_2 is one of the representative photocatalysts used, for example, to purify water and air. In order to enhance the activity of the TiO_2 photocatalyst, Pt nanoparticles are often deposited on the surface[1]. In this study, we aimed to investigate the photodeposition process of Pt nanoparticles on TiO_2 using Pt L_3-edge XAFS spectroscopy focusing on the bonding states of Pt on TiO_2 surface and local structures around Pt atoms.

Before irradiation, the feature of Pt L_3-edge XANES spectrum of the TiO_2 sample adsorbing the Pt precursor was similar to that of PtO_2. The energy position of the main peak of XANES shifted to lower X-ray energy with the photoirradiation time, indicating a decrease in the ratio of Pt^{4+} ions by reduction.

All XANES spectra were reproduced with the linear combination of two XANES spectra of PtO_2 and Pt metal, and the fractions of Pt^{4+} and Pt^0 for all the Pt/TiO_2 samples were directly evaluated. Fig.1 shows irradiation-time dependence of edge jump intensity at 11740 eV and the fraction of Pt^0. The edge jump intensity corresponds to the deposited Pt concentration.

Before photoirradiation, only 20% of Pt^{4+} ions were adsorbed on TiO_2. The Pt^{4+} ions increased to 45% by photo-assisted adsorption after 5 minutes, in which most of the adsorption sites of Pt on the TiO_2 surface would be occupied. Subsequently, the adsorbed Pt^{4+} ions were gradually reduced during the following 5 to 20 minutes of photoirradiation. In the successive period for 20–30 min, the amount of the adsorbed Pt^{4+} ions drastically increased and the reduction of Pt^{4+} to Pt^0 drastically occurred. After that, the fraction of Pt^0 gradually increased by further photoreduction.

Author Index

Bold page numbers indicate presenter