3.2 First-Principles Calculation of Material Properties

Atomic Structures and Electronic Properties of Hard- and Soft-Nanomaterials

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Main purpose of this project is to develop the density-functional approach which enables us to perform more accurate and larger scale static and dynamical calculations on massively parallel architecture computers, to clarify underlying physics and chemistry in phenomena in nano-materials and structures, and to predict new phenomena in nanoworld. The following is two examples which we have achieved in 2014 fiscal year.

1. Magnetic Ordering without Magnetic Elements on SiC Nanofacet

Nanometer-scale structures are now accessible. Common expectation that such nanostructures break through limitations of current technology may rely on a fact that nano-scale shapes affect wave-functions of relevant electron states. However, a way of designing nano-shapes which decisively affect the electron states and therefore are intriguing in science and useful in technology is lacking. Our calculations based on the densityfunctional theory (DFT) developed by the realspace scheme (RSDFT code) [Iwata et al., PRB 77, 115208 (2008); J. Comp. Phys. 229, 2339 (2010); Hasegawa et al., Int. J. HPC Appl. 28, 335 (2014)] show that peculiar electron states which are localized near but extended along step edges of the nano-facets of SiC exhibit either ferromagnetic (FM) or anti-ferromagnetic (AFM) spin polarization. Considering that SiC is an emerging material in the power electronics and that spin current is the new non-dissipative carrier for the information in future, this finding based on our RSDFT scheme has great impact.

Figure 1 shows the most stable nano-facet structure on SiC (0001) surface which we have found in our RSDFT calculations. We have found that the nano-facet structure is a bunched single bi-layer atomic steps and that the balance between the stepstep repulsive energy and the surface-energy gain on the terrace causes the appearance of a particular shape of nano-facet: The facet angle φ which is the angle between (0001) and the experimentally



Figure 1: A side views of the $(11\bar{2}n)$ (n = 12)nanofacet with the facet angle $\varphi = 15.3^{\circ}$ on the 4H-SiC(0001) vicinal surface. Green, yellow and purple balls indicate the Si, C and H atoms, respectively. The labels such as T_p^{Si} denote several particular sites which may be passivated by hydrogen.

observed $(11\overline{2}n)$ is almost common (magic angle, $\varphi = 12^{\circ} - 16^{\circ}$) and the height of the nanofacet along the (0001) direction is a integer or a half-integer of the unit-cell height [1].

We have found that step-edge localized states (Fig. 2) appear below Fermi level $(E_{\rm F})$ which show flat dispersion along the step edges. As is clear from Fig. 2, this flat-band states have a chemical character of dangling bonds of the edge C atoms. The dangling bonds of Si edge atoms constitute other states near $E_{\rm F}$ due to the lower electron affinity of Si.

Hydrogen adsorption is a common process to fabricate semiconductor devices. We have found that atomic sites on the terrace and the step edges shown in Fig. 1 exhibit different hydrogen-philicity: The step edge C atoms and then some edge Si atoms exhibit less adsorption energy of hydrogen atoms. Hence, it is likely that the terrace Si atoms and other edge Si atoms are H-terminated. In this situation, the flat-bands come up at $E_{\rm F}$ and show spin polarization.

Our RSDFT calculations actually show that the ground state is either ferromagnetic or antiferromagnetic and the spin density is distributed



Figure 2: Expanded views of the Kohn-Sham orbital of the flat-band edge states localized near C atoms at the edges. The top and side views are displayed in (a) and (b), respectively. The red and blue colors depict positive and negative values, respectively, of the Kohn-Sham orbitals. The dashed line in (a) shows the step edge position.

solely along the step edges of the nanofacets. We predict that control of H-adsorption controls the filling of the flat-band stets and then the distribution of the spin density in the magnetic states.

2. Stability and Gap Modulation through Atomic Protrusion in Bilayer Silicene

Bilayer graphene provides new aspects of graphene physics such as the band gap opening and moiré-pattern-induced electron localization. The interlayer interaction is obviously weaker than the intralayer interaction but decisive to modulate the electron states due to its symmetry breaking. Similar intriguing behavior with the extension related to the spin-degrees of freedom is expected for layered Si (silicene), which has been grown experimentally with forms of monolayer and of a few layers mainly on Ag substrates. One of the most important characteristics which discriminate silicene from graphene is the buckling of two sublattices caused by the preference of Si for sp^3 hybridization. In fact, first-principles calculations within the local density approximation have clarified that a planar Si monolayer is unstable to the buckling, and that the resultant freestanding monolayer silicene with the buckling of 0.44 Å have the Dirac cone at the Fermi level, $E_{\rm F}$. This buckling brings about a complex but rich variation in structure and electronic properties in bilayer silicene.

We have performed systematic first-principles total-energy and phonon calculations for freestanding bilayer silicene with various lateral periodicities and atomic densities [3]. By extensive geometry optimization followed by the phonon calculations, we have unequivocally identified ten dynamically stable structures with distinct atomic configurations, symmetries, and periodicities. We have clarified that the ten structures include all the six structures reported in the past. Other four structures are newly found and more stable than the previously reported ones. We have found that the more stable structures have a single prominent structural characteristics, i.e. the protrusion of Si atom. We have also found that there is an energetically optimum lateral periodicity for the protruded structure, i.e., $\sqrt{3} \times \sqrt{3}$ or 2×2 , depending on the stacking of the two Si layers. We have further clarified that the stable freestanding bilayer silicene is a semiconductor in which the energy gap is sensitive to the detailed protruded structure.

The calculated total energies of freestanding bilayer silicene with various stackings and periodicities [3] show that the hex-OR- 2×2 structure newly found here has the lowest energy, and the slide- 2×2 follows with the total-energy increase of 6 meV/atom. The OR- $\sqrt{3} \times \sqrt{3}$ and rect-OR- 2×2 structures are also close in energy (+9 and +10 meV/atom from the lowest energy,The $AA-\sqrt{3} \times \sqrt{3}$ and $AA-2\times 2$ respectively). are in the second lowest energy group (+31 and+41 meV/atom, respectively). The OR-, AA-, slide-, AB-1×1 structures have relatively high energy (+60, +78, +112 and +131 meV/atom, respectively) compared to the $\sqrt{3} \times \sqrt{3}$ and 2×2 structures.

Related Publuications

- K. Sawada, J.-I. Iwata and A. Oshiyama, "Magic Angle and Height Quantization in Nanofacets on SiC(0001) Surfaces" Appl. Phys. Lett. **104**, 051605 (2014).
- K. Sawada, J.-I. Iwata and A. Oshiyama, "Spontaneous Appearance of Low-dimensional Magnetic Electron System on Semiconductor Nanostructures" arXiv:1504.06934.
- Y. Sakai and A. Oshiyama, "Structural Stability and Energy-Gap Modulation through Atomic Protrusion in Freestanding Bilayer Silicene" Phys. Rev. B (R) (2015) in press.

Hydration effects on ligand binding to NylB enzyme

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Arthrobacter sp. KI72, which is a bacterium found in the waste of a nylon factory, utilizes nylon oligomers as sole carbon and nitrogen sources for their growth [1]. Nylon hydrolases, NylB, have been extensively performed to enhance the hydrolysis activity both by experimental and theoretical works. According to the X-ray crystallographic analyses, NylB has two different forms, i.e. the substrate-free form (open form) and the substrate-bound form (closed form). To form the later structure, a loop-segment drastically moves towards the substrate showing the induced-fit mechanism. However there is no quantitative information about how much the substrate-enzyme complex is stabilized due to both the amino acid residues participating the induced-fit and the surrounding water molecules.

In this project, fragment molecular orbital (FMO) calculations have been successfully applied to NylB in order to investigate hydration effects on an enzyme-substrate binding structure.

(Statistically corrected) Inter-fragment interaction energy analyses on this system quantitatively characterise the interaction between an aminohexanate dimer (ALD) and amino acid residues such as Asp181, Ser112, and Ile 345, in NylB, which is considered important residues for constructing enzymesubstrate complex. Furthermore, we show that the direct interaction between ALD and NylB weakens by hydration because water molecules cause charge translation or polarization to ALD or each amino acid residue, but including interaction energy between ALD and water molecules, this complex are stabilized largely. This result indicates the hydration effects are of great importance in forming the enzymesubstrate complex [2].

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First-principles simulations of atomic geometries, electronic properties and chemical reactions at interfaces

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Adsorption and reaction of CO_2 on metal surfaces are fundamentally important in surface chemistry and other related fields [1,2]. Previous studies of CO_2 adsorption on singlecrystal Cu surfaces have shown that on flat copper surfaces, CO_2 is weakly adsorbed molecularly and needs high activation energy to dissociate: 0.69 eV for Cu(110)[3]. On the Cu(311) surfaces, Fu and Somorjai found that CO_2 is adsorbed and dissociates to CO and O with a 4 L dose at 150 K using temperature



Fig. 1. Schematic of CO_2 dissociation followed by Cu-O-Cu chain formation on Cu(221) surface. IS, TS, FS, and IM represent initial, transition, final, and intermediate states, respectively. programmed desorption (TPD) experiment [4]. Boenicke *et al.* showed by means of thermal desorption spectroscopy (TDS) experiment that CO_2 is chemisorbed and dissociates at 95 K over the Cu(332) surface[5]. Recently, Koitaya and co-workers showed that CO_2 dissociation takes place on the stepped Cu(997) surface rather than on flat Cu(111) surface at 83 K by using infrared reflection absorption spectroscopy (IRAS) [6]. Meanwhile, it is not clear whether CO_2 dissociation takes place on

> Cu surfaces at low temperature theoretically. Thus, we studied the dissociative adsorption of CO_2 on the Cu(111), Cu(221), Cu(211), and Cu(11 5 9) surfaces by using state-of-theart density functional theory

(DFT) [7]. We obtained that the barrier energy for CO_2 dissociation on the flat Cu(111) surface is 1.33 eV. While, the barrier energies on stepped and kinked surfaces are 1.06 eV, 0.67 eV, and 1.02 eV for the Cu(221), Cu(211), and Cu(11 5 9) surfaces, respectively. Even though the activation energy is 0.66 eV lower on the stepped Cu(211) surface than on the flat Cu(111) surface, we concluded that CO_2 does not dissociate on ideal flat, stepped or kinked Cu surfaces at low temperature.

We also studied the effect of Cu adatoms and water molecule in the CO₂ dissociation. We propose that the CO₂ dissociation is followed by the Cu-O-Cu chain formation (Fig. 1) with 0.46 eV barrier energy. By introducing water molecule impurity, CO₂ dissociation takes place via hydrocarboxyl (COOH) intermediate with 0.48 eV barrier energy. According to these results, additional factors on the Cu surface such as adatoms and/or gas phase impurity, which can be found in "real" experiment condition, are important to enhance CO₂ dissociation.

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Theoretical study on the cohesive properties of organic solids with the van der Waals density functional

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Organic semiconductors have attracted a lot of attention as a component of the organic (opt)electronics, owing to their advantages, such as low-cost fabrication processes, flexibility, and low-power consumption. Their relevant electronic properties, such as charge transport, are determined not only by the electronic structures of constituent molecules, but also by their conformation and configuration. The theoretical treatment of organic semiconductors remains challenging, as the semilocal density functional theory fails to describe the dispersion forces accurately.

Here, we study the cohesive properties of organic semiconductor crystals using the van der Waals (vdW) density functional (vdW-DF), which describes the vdW interaction in molecular complexes or solids correctly at a reasonable computational cost [1,2]. We use a revised vdW-DF recently proposed (rev-vdWDF2) [3]. The calculations are done with the Vienna Abinitio Simulation Package (VASP) [4] on the supercomputer system B in ISSP. We use 64-256 cores (Job class: F16-F64) depending on the unit cell size.

We examine the stable α - and β - polymorphs of Zinc-Phthalocyanine (ZnPc) crystal. The lattice constants of β -ZnPc optimized with revvdW-DF2 are found to agree with experiments within 1 %. For α -ZnPc, we optimize the geometry by using the experimental value of α -CuPc as an initial guess.

The bandwidth of the highest-occupied

molecular orbital (HOMO)-derived band is estimated to be 64 meV. It is in fair agreement with the recent high-resolution angleresolved photoelectron spectroscopy (ARPES) measurement (92 meV) [5].

To clarify the origin of the slight band dispersion, the HOMO bandwidth (W) is calculated when (a) the intermolecular distance b between the two molecules in the unit cell is changed, or (b) the angle $\theta_{\rm mol}$ between the crystal axis and the normal of the molecular plane is changed. W is found to be sensitive to the intermolecular distance and the molecular orientation angle. Furthermore, by examining the Maximally-Localized Wannier Function (MLWF) [6] and estimating the transfer integral, we find that the HOMO dispersion is dominated by both the nearest- and second nearest-neighbor transfer integrals. The molecular configuration becomes most stable when the HOMO band energy is minimized, as a result of the balance between the antibonding and bonding interactions. The study demonstrates the roles of the inter-molecular distance and the molecular tilt angle in the formation of the band structure, and the importance of the accurate description of the crystal structure [7].

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DFT free energy analysis of redox reaction mechanisms at interfaces in batteries and catalysts

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Our focus is on (1) development and/or establishment of theories and computational methods for problems in electro and interfacial chemistry based on the "density functional theory (DFT), and (2) understanding reaction mechanisms at interfaces in (photo)catalysts, photovoltaic cells, and batteries for universal interface science.



Initial Stage of Charging (Li ion concentration) Fig. 1. Schematic picture of space-charge layer mechanism at interface between the oxide cathode and sulfide electrolyte, and the buffer layer effect.



Fig. 2. Interfacial states of (left) dyesensitized solar cell and (right) perovskite solar cell elucidated in our works.

In this year, we have elucidated several novel reaction mechanisms in Lithiumion batteries (Fig. 1) [1,2], dye-sensitized solar cells & perovskite solar cells (Fig. 2) [3,4,5], CeO₂ & diamond catalysts [6,7] as well as developed a new method for donor-acceptor electron transfer based on Marcus theory and DFT [8].

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First-principles meta-dynamics analysis in Catalytic Referred Etching method Reaction barrier in etching of GaN, SiC and SiO₂

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We investigated chemical etching reaction processes in Catalyst Referred Etching (CARE) surface finishing method by which step-and-terrace shaped smooth surfaces can be formed by wiping the surface by a catalyst plate in an etching solution [1]. It has been reported by experimentalist that crystalline SiO₂ can be smoothened by using water etchant with Pt catalyst. In this project, we analyzed this etching process and the role of Pt catalyst in an atomic scale by using firstprinciples reaction barrier calculations with STATE code [2]. Figure 1 shows applied α quartz SiO₂ step-surface model with OH terminated and with and without Pt (111) slab.



Fig. 1: Calculation model .



Fig. 2: Energy profile in dissociative adsorption.

We calculated the reaction process of dissociative adsorption of H_2O at SiO_2 surface initially placed on SiO_2 surface as the initial stage of etching reaction process by using NEB method. NEB calculation is performed by using multi-replica MPI calculation. The energy profile (Fig. 2) indicates that the reaction barrier height is reduced in the model with Pt slab. The analyzed barrier height reduction mechanism will be published elsewhere.

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Exploratory study on electric field effect of the magnetic anisotropy in the spintronics material with the oxide layer

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We investigated the structural, electronic, and magnetic properties in the slab of interface $Fe/SrTiO_3(001)$. It was found that such interface has a large electric field effect on magnetic anisotropy. This may come from the property of a large dielectric constant in $SrTiO_3$. We obtained a negative slope in the EF variation of magnetic anisotropy energy (MAE). This showed a contrast with the system measured in the previous experiments, in which the latter had a positive slope in Fe/MgO systems.

The development of the memory which utilizes magnetic resistivity, random magnetic access memory (MRAM), has been carried out very actively in spintronic applications. The heat energy dissipation remains as a critical problem in the process of magnetization reversal. To solve such problem, reduction on the energy barrier external electric field (EF) is by considered to be a promising solution. Thus, the system having a large EF effect on MAE has been desired. In one of such approaches, the high-K material of a large dielectric constant, such as $SrTiO_3$ (STO), can be useful to the insulating separator in the magnetic memory cell.

For the slab of Fe(3ML)/TiO₂/SrO/TiO₂, in which the interface Fe atom was placed to the next of O atom, we carried out first-principles

calculation which employs the density functional theory (DFT) and fully relativistic ultrasoft pseudopotentials. Energy cutoffs for electron density and wavefunction are 300Ry and 30Ry respectively. We used the (32, 32, 1) mesh of k space sampling. The generalized gradient approximation was adopted for exchange correlation energy. The structural optimization was performed by using atomic forces except the in-plane lattice constant. For the lattice constant, we fixed the value extracted from the bulk STO, which is slightly smaller than those of Fe and MgO. The ESM method with zero external EF condition was used to avoid artificial built-in EF in the repeated slab model; vacuum/Fe STO/vacuum/ESM. For both vacuum layers, the width of 5.29Å was taken. We used the program code house-made which was parallelized in sampling k-point, applying it to System B in ISSP.

We estimated MAEs for the external EF. Due to the Fe-O bonds at the interface, the system showed a large perpendicular magnetic anisotropy (about 1.2 mJ/m² of MAE). The MAE increased when applying an EF of electron accumulation condition at the interface. The rate was obtained to be 7.3 fJ/Vm with respect to the external EF. The system Fe/STO was found to be a good candidate of both perpendicular magnetic anisotropy and large EF effect.

Analyses on atomic structure, magnetism, and electronic structure in spintronics materials

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We performed the first-principles density functional calculation of the slab systems, MgO(5ML)/Fe(5ML), Fe(5ML)/MgO(5ML)/Fe (5ML), and MgO(3ML)/Fe(3ML)/MgO(1 or 7 ML). We investigated structural and electronic properties in the Fe/MgO interfaces. The slab of a tunnel junction Fe/MgO/Fe exceptionally has a short Fe-O distance and a large Mg displacement from the O layer. In the junction with a small in-plane lattice constant, the interface resonance state tends to shift to a low energy, resulting in a partially electronoccupied state.

For the slab models, we used the generalized gradient approximation for the density functional theory (DFT), and the ultrasoft pseudopotentials. Energy cutoffs for electron density and wavefunction are 300Ry and 30Ry respectively. We used the 24x24x1 mesh of k space sampling. We optimized electronic wavefunctions and atomic positions by minimizing the total energy functional. The structural optimization was performed by using atomic forces except the in-plane lattice constant. For each slab system, the two lattice constants extracted from Fe and MgO bulks were employed. We used the house-made program code which was parallelized in sampling k-point, applying it to Systems B and C in ISSP.

We estimated the layer distances in the

Fe/MgO interface and in the Fe layer, and calculated the partial density of states (PDOS) projected on the Fe at the interface. We usually obtained the rigid Fe-O bond, the Mg displacement, and the interface resonance state (IRS) just above EF. The Fe/MgO/Fe slab exceptionally showed the differences in the layer distances around the interface between the slabs with MgO and Fe lattice constants and tended to have the partial occupied IRS.

The PDOS of $d(x^2-y^2)$ largely depended on the slab. This PDOS forms a peak around EF, however the peak is smaller than those of d(xy)and d(yz+zx). This is because the $d(x^2-y^2)$ orbital extends to the neighboring Fe atoms within the Fe plane, while the orbitals of d(xy)and d(yz+zx) to the directions that have no covalent bond in the interface. We also observe small minority-spin states in d(yz+zx) and $d(x^2-z)$ y^2) at just below (-0.2 eV) and above (0.25 eV) Fermi level, respectively, the in the MgO/Fe/MgO slab, but these states smear out in the Fe/MgO/Fe and MgO/Fe slabs. As well as the IRS, the variation in location of $d(x^2-y^2)$ could be a key to control of electronic and magnetic properties in the interface.

The properties obtained in this calculation will be available to a fine control in a fabrication process of the interface and an improved design in the magnetic material for an EF-driven device.

Analyses on atomic structure, magnetism, and electronic structure in spintronics materials and molecular magnets

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We investigated the electric field (EF) effect on the interface magnetic anisotropy of a thin MgO/Fe/MgO layer using density functional theory (DFT). The perpendicular magnetic anisotropy energy (MAE) increased not only under electron depletion but also under some electron accumulation conditions, showing a strong correlation with the number of electrons on the interface Fe atom. The reverse variation in the MAE under the EF was ascribed to novel features on the charged interface, such as electron leakage. We discussed the origin in terms of the electronic structures [1].

In magnetic tunnel junctions, duplication of a single junction has been introduced to improve performance. Similarly, in a magnetic device intended to exploit the EF-driven change in the magnetic anisotropy, a proposed double interface structure has shown a large enhancement in the EF-induced effect on the MAE. In the experiment, the researchers found unusual nonlinear behavior of the EF dependence of the MAE. For both electron depletion and electron accumulation conditions at the interface of the magnetic metallic layer, the MAE changes to favor stability in the magnetic direction perpendicular to the interface plane. The origin of this preference in such a double interface structure was not yet clear. The establishment of nonlinear behavior in the MAE variation may extend the range of applications of EF-driven magnetic devices. A theoretical understanding of the behavior will accelerate development. In the present calculation, we successfully obtained this behavior using a realistic model with a double interface, while MAE variation had been investigated theoretically only single at interfaces.

We used a slab system, vacuum (0.79 nm)/MgO [4 atomic monolayers (ML)]/Fe (3ML)/MgO (7 ML)/vacuum (0.79 nm). We carried out a first-principles density functional calculation that used fully relativistic ultrasoft pseudopotentials and a planewave basis by using the generalized gradient approximation. The MAE was estimated from the total energy difference between the [100] (x-axis) and [001] (z-axis) magnetization directions, that is, MAE =E[100]-E[001]. We used a 32x32x1 mesh in k point sampling, and the in-plane lattice constant was fixed at the value for the MgO layer extracted from the bulk. We used the housemade program code which was parallelized in sampling k-point, applying it to Systems B and C in ISSP.

The MAE data calculated and variation rate with respect to the EF were in good agreement with the experimental data. The important results were summarized to two points: obtaining the non-linear dependence of MAE and a good agreement with the experimental result on the EF variation rate of MAE. Property of the non-linear dependence was found to correlate with the number of electrons on the Fe atom at the interface which the EF was imposed on. We investigated the partial density of states (PDOS) projected to the 3d orbitals on the Fe atom at the interface. We obtained the localized electronic states of Fe 3d orbitals just above the Fermi level. They were found to extend to the directions where the covalent bond was not formed at the interface, and also found to correspond well to the interface resonance state (IRS) observed in experiment.

In our model system, the negative slope of the MAE variation at a finite negative EF was understood to represent electron leakage from the interface to the MgO(R) layer, particularly to the surface adjacent to the vacuum layer. In the real system, the existence of charging spots (places where electrons are trapped) in the MgO(R) layer may be needed to explain the observed negative bias voltage. There could be an impurity site or a defect site in such systems.

The existence of charging spots was consistent with the fact that the variation in the number of electrons was reduced on the interface at EFs below Ec where the MAE had the minimum value. The number of negative charges at the charging spots increased as the external EF decreases, reducing the effective EF imposed on the Fe/MgO(R) interface. In addition, another candidate for charging spots is an IRS at another MgO/Fe interface. This IRS should be assumed not to contribute to electron conduction along the perpendicular direction. In the previous experiment, there was an Fealloy/MgO/Fe junction, in which the IRS at MgO/Fe may act as a charging spot when negative voltages are applied, supposing that the IRS forms a set of localized states (nonconducting states). The theoretical base obtained highly encourages experimental research.

Other than the calculation of EF variation of MAE, we calculated the following topics; electronic structures in Tl/Si(111) and Tl/Si(110), structural properties in the pair of Fe phthalo-cyanine (FePc) molecules, and stress calculation of the van der Waals density functional method.

The rest of this report is devoted to the results on van der Waals density functional (vdW-DF) method [2]. In this method, the options of atomic forces and cell stresses were introduced. Concerned with magnetic systems, we obtained systematically good results in the calculations of the solid oxygen. The new functional for vdW spin-polarized density functional method, which was developed and investigated for magnetic materials in the last year, was applied to solid oxygen. The crystal structural data of solid oxygen at ambient pressure was examined. The results of LDA and GGA differed largely from the respective experimental data, however, the vdW-DFs much improve the structural data, particularly, the equilibrium volume agrees well with the experimental data. The magnetic energy, defined by the total energy difference between the antiferro- and ferro-magnetic states, was found to be comparable to the energy gain from vdW interaction in the equilibrium crystal structure. It is important as a next step that the extension to spin-polarized materials of vdW-DF is applied to both the study of solid oxygen under high pressure and the application of magnetic systems other than oxygen system in order to verify the effectiveness of vdW-DF.

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Atomic structures, structural stabilities, and electronic properties of impurity-doped carbon-based materials

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Since its discovery, graphene, a monolayer sheet of graphite, has received a lot of attention from nanoscience and nanotechnology. The few-layered sheets of graphene have also attracted great attention since they exhibit different electronic structures from monolayer of graphene.

One of the effective ways to tune the electronic properties of carbon-based nanomaterials is to dope them with foreign atoms. There have been several studies on doping with boron (B) and nitrogen (N) into monolayer graphene. Actually, the chemical doping with B and N atoms can modify the electronic properties of graphene, and therefore chemically doped carbon nanomaterials are applied to developments of nanoelectronics, sensors, storages, etc. However, our knowledge as to B and N doping into bilayer graphene is still limited at present.

Here, we report energetics of B-doped and N-doped bilayer graphenes with AAand AB-stacking patterns using first-principles electronic-structure calculations within the density-functional theory. It is found that B and N-doped bilayer graphenes stacked with AA pattern are energetically favorable than those stacked with AB pattern. It is also found that the formation energies for N-doped ABstacking bilayer graphene depend on dopant sites, whereas those for B-doped ones show almost the same.

To discuss the energetics of B- and N-doped bilayer graphenes, the formation energy is defined by

$$E_{\rm f} = E_{\rm tot} - m_{\rm C}\mu_{\rm C} - \mu_{\rm BorN},\qquad(1)$$

where E_{tot} is the total energy of the B- or

N-doped bilayer graphene with AA, AB1 and AB2 stacking patterns, $m_{\rm C}$ is the number of C atoms in a supercell, and $\mu_{\rm C}$, $\mu_{\rm B}$ and $\mu_{\rm N}$ are the chemical potentials of pristine bilayer graphene with corresponding AA or AB staking pattern, α -boron crystal, and N₂ molecule, respectively. Here, AB1 stacking is that the C atom on top of the C atom of the adjacent graphene layer is replaced with a dopant, and AB2 stacking is that the C atom on top of the adjacent graphene layer is replaced with a dopant.

The formation energy of substitutional B doping into AA-stacked bilayer graphene is 1.36 eV, which is found to be the smallest among doping sites into three kinds of stacking patterns AA, AB1, and AB2. In the case of the substitutional N doping, the formation energy is the smallest value of 0.24 eV for the AA stacking. In addition, our calculated formation energies of monolayer graphene doped with B and N atoms are found to be 1.42 eV and 0.32 eV, respectively [1]. The B- and N-doping into AA-stacked bilayer graphene are found to be energetically favorable compared with those into monolayer graphene [2].

In the case of B doping into AB-stacked bilayer graphene, the formation energies for AB1doping site is similar to that for AB2 site by only 6 meV difference. On the other hand, in the case of the N-doped graphene, AB1stacked graphene has the considerably larger formation energy (by 28 meV) compared with AB2 stacking, indicating that the substitution with N atom on top of the center of a hexagon becomes energetically favorable rather than that on top of C atom. Thus, the formation energy for the substitution with N atom depends on the substitution site, whereas that for B atom does not depend on it.

In summary, we have studied energetics of B-doped and N-doped bilayer graphenes with AA and AB-stacking patterns using firstprinciples density-functional calculations. The formation energy results suggest that the B and N dopings into AA-stacked bilayer graphene become energetically the most favorable among three types of stacking patterns AA, AB1, and AB2. It is found that the formation energies for N-doped AB stacking bilayer graphene depending on N-doped sites, whereas those for B-doped ones show almost the same values.

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First-principles calculation of interactions between extreme pulse light and matter

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In recent optical sciences, measurements in time domain using extremely short laser pulses have been developing. Nonlinear phenomena utilizing extremely intense laser pulses have also been attracting interests. We have been developing a first-principles computational method to describe interactions between pulsed light and solids based on real-time timedependent density functional theory. We solve the time-dependent Kohn-Sham equation in real time and real space for electrons in a unit cell of crystalline solids where the electric field of pulsed light is treated as spatially-uniform, time-dependent vector potential.

We have applied our method to analyze several experimental measurements employing extreme light pulses. One is the analysis of ultrafast electric current produced at a surface of transparent materials irradiated by a strong and ultrashort laser pulses. We have analyzed electric current produced in the surface of crystalline SiO_2 and found that measured features such as critical intensity and dependence on carrier envelope phase are well reproduced by our calculations [1]. We also applied our method to experiments exploring ultrafast changes of band gap of silicon under irradiation of a strong, a few cycle optical field. Our calculations show that the carrier generation by the pulsed light is caused by tunneling mechanism, and provide time evolution of orbital wave functions which may be used as an input for the analysis of attosecond transient absorption [2].

Electron dynamics calculations employing uniform spatial grids are robust but time consuming. We have investigated a possible basis expansion method which may provide accurate description with much less computational resources. We have confirmed that the basis expansion method works if we employ occupied orbitals of nearby k-points as well as those of the original k-point [3].

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Ab Initio Study of Excited Electronic States and Nonadiabatic Processes of Nanostructures under External Fields

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In the project we investigated the following five topics this year. 1) Laserassisted field emission from silicene nanoribbons by time-dependent density functional theory (TDDFT), 2) low-energy electron wavepacket scattering with graphene flakes (GFs) by TDDFT, 3) nanoplasmon dynamics and field enhancement of GFs by TDDFT, 4) positron states at a lithium-adsorbed Al(100) surface by two-component DFT (TC-DFT), and 5) nonadiabatic couplings by TDDFT and charge-transfer excitation energies by a perturbative approach.

1) Laser-assisted field emission from silicene nanoribbons by TDDFT[1]: We investigate laser-assisted field emission (LAFE) from a silicene nanoribbon (SiNR) using TDDFT simulation. The emission mechanism in the present study is considered to be over-barrier photo to be governed by electronic dipole transitions, the characteristics of the excited states, and the energy levels of the excited states relative to the potential hump. The qualitative features of emission from the SiNR are similar to those from graphene nanoribbons (GNRs). The emission currents from SiNR, however, are found to be much larger than those from GNR for the same laser parameters in spite of a larger work function for SiNR. We reveal the emission currents in real time and space on an atomic scale, and observed current being driven back and forth in the early stage of emission. We further elucidate the dynamical correlation among the laser pulse, the Kohn-Sham potential and emission currents wiggling under the ponderomotive force. We further explored the electronemission dynamics under lasers of lower energies and higher powers than those of the simulations above and found a signature of carrierenvelop phase effect and phenomena of multistep photo absorption by Kohn-Sham decomposition technique. These are still under investigation. Large-scale TDDFT calculations have been performed using System A.

2) Low-energy electron wavepacket scattering with GFs by TDDFT[2]: Low-energy electron scattering with GFs is investigated using a TDDFT simulation in real time and real space. By representing the incident electron as a finite-sized wave packet, we obtain diffraction patterns that show not only the regular features of conventional low-energy electron diffraction (LEED) for periodic structures but also special features resulting from the local atomic inhomogeneity. We have also observed π plasmon excitation upon electron impact on a GF. These results have been reported in Ref. 2. We further investigated the detailed properties of electron scattering from GFs and recently found a signature of secondary electron emission (SEE). We continue the simulations to elucidate the mechanism of SEE. Large-scale TDDFT calculations have been performed using System B.

3) Nanoplasmon dynamics and field enhancement of graphene flakes by TDDFT[3]: We investigate nanoplasmon dynamics in GF monomers and dimers using real time and space time-dependent density functional theory. By showing the characteristic features of dynamical polarizability, we verified that the two distinct peaks in the optical absorption spectra can be attributed to π and $\pi + \sigma$ plasmons. We clearly show a significant difference between on- and off-resonance responses of the π plasmon by demonstrating the spatial distribution of induced charge and the electric field. We thus reveal the mechanism of plasmon-induced field enhancement near GF edges, which shows great importance of first-principles study on molecular nanoplasmonics.

4) Positron states at a lithium-adsorbed surface by TC-DFT[4]:Al(100)The positron surface state and the energetics for positron reemission are investigated using two-component density functional theory (TC-DFT) in the projector augmented-wave Trapping of positrons by the framework. surface image potential and the effect of the positron band-shift energy in the surface region are appropriately described by the corrugated mirror model and the ramp potential, respectively, without empirical parameters. The results obtained for various physical quantities of positron states on a clean Al(100) surface, *i.e.*, the affinity, work function, life-time, binding energy, and activation energy, are in good agreement with the experimental results. The positron states on Li-adsorbed Al(100) surfaces are highly dependent on the Li coverage. In particular, the work function of positronium negative ions (Ps⁻) becomes negative at low Li coverage, which indicates the possible emission of Ps⁻ from the adsorbed surface. The present study not only elucidates the key energetics that are responsible for positron reemission from the surface, but also emphasizes the excellent performance of TC-DFT for prediction of the positron state on real surfaces.

5) Nonadiabatic couplings by TDDFT and charge-transfer excitation energies by a perturbative approach: Nonadiabatic couplings (NACs) between excited states were calculated using the frequency-domain TDDFT. The many-body wave functions of the excited states were constructed from the TDDFT expression of matrix elements between ground and excited states, using the Casida ansatz. In particular, the known problems in the application of the Casida ansatz in the literature were removed by considering the difference of the operators and adopting a method to avoid the accuracy problem due to the nonlocal pseudopotentials. We performed evaluation of both the first-order and second-order NACs in H_3 near the conical intersection between the first and second doublet excited states. For the first-order NACs, the integral of angular NACs over a circular contour was shown to give a value quite close to the geometric phase of π . For the second-order NACs, the Cartesian components were shown to become large when approaching the intersection point and cannot cancel each other out in the sum. To calculate charge-transfer excitation energies which are severely underestimated by TDDFT within LDA or GGA, we implemented a perturbative approach based on DFT, which does not need the self-consistent calculation as required in Δ SCF and thus can avoid the variation collapse in Δ SCF due to charge sloshing. Benchmark calculations confirmed the usefulness of our implementation in the planewave pseudopotential framework when the molecular systems become large. Parallelized computing has been performed on System B.

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Parallelized ultra-large-scale electronic-structure theory based on first principle calculation and novel numerical method

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The program code 'ELSES' (http://www.elses.jp) were developed for order-N massively parallel electronic structure theory on the ISSP supercomputer System B. A mathematical foundation is novel solver algorithms with Krylov subspace theory for the generalized shifted linear equations, in the form of (zS-H) $\mathbf{x} = \mathbf{b}$. Practical calculations were carried out with modelled (tight-binding-form) Hamiltonians. Several mathematical studies were also carried out as related methodologies.

A recent paper [1] gives a benchmark of amorphous-like conjugated polymers with upto one-hundred million atoms on the K computer. The K computer was used with upto the fullcore calculations. The MPI/OMP hybrid parallelism is used.

As mathematical studies, we studied the convergence behavior of the block-Jacobi based massively parallel eigenvalue solver we developed last year both theoretically and experimentally [2]. We also developed basic



Fig. 1: A preliminary calculation of a bundled conjugated polymer (polyphenylene vinylene, PPV) with N = 117,962 atoms. The length of a polymer is approximately 40 nm.

techniques to extend our algorithm to deal with the singular value decomposition and made some preliminary performance evaluation [3][4].

As applications, organic materials were calculated preliminary, such as bundled conjugated polymer (Fig.1) [5]. Moreover, optimally hybrid numerical solvers were constructed for massively parallel generalized eigenvalue computations [5], in which a routine is chosen for each subprocedure from the three parallel solver libraries of ScaLAPACK, ELPA[6] and EigenExa [7]. The strong scaling benchmark was carried out on the K computer for electronic structure calculation problems in the matrix sizes of $M = 10^4 \cdot 10^6$. As results, the two newer libraries, ELPA and EigenExa and their hybrid give better benchmark results than the conventional ScaLAPACK library. The benchmark with the ISSP supercomputer system B was carried out with smaller matrix sizes of $M < 10^5$, because the benchmark was carried out by regular job class in which the largest number of nodes is 256.

The present project was carried out in collaboration, mainly, with Susumu Yamamoto (Tokyo University of Technology), Tomohiro Sogabe, Takafumi Miyata, Shao-Liang Zhang (Nagoya University), Yusaku Yamamoto (University of Electro-Communications), Hiroto Imachi (Tottori University).

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Nudged elastic band method with constant bias potential

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An electrochemical reaction at the electrode-electrolyte interface is one of the most important issues on performance and durability of energy harvesting devices such as a fuel cell, a secondary battery, a photovoltaic cell and a photoelectrochemical cell. We have been trying to understand the electrochemical reaction by developing a method called effective screening medium (ESM) method [1].



Fig.1 (a) H atom diffusion on Al(001) surface. (b) The energy profile and the variation of the excess charge of the surface along the path with constant- μ calculation.

Recently, we have successfully developed an extension for the ESM method [2], in which we can control the bias potential applied to the interface. In contrast to the convectional method, we need to discuss the following grand potential instead of the total energy:

$$\Omega = E_{\rm tot} - \mu n_{\rm FCP}$$

We demonstrated the constant bias method combined with the nudged elastic band method [3]. We calculated a hydrogen atom diffusion of Al(001) surface. As shown in the figure 1, the energy profile of the diffusion and the amount of charge depends on the applied potential.

This constant bias method allows us to simulate bias dependent atom diffusion in electrochemical system.

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Adsorption and Clustering of Metal Atoms on Organic Molecular Semiconductors

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Organic molecular semiconductors are key materials for future optical and electronic devices because of their unique characteristics such as softness and light mass. During the device fabrication, a variety of impurity metal atoms are often incorporated into semiconductor layers and they are believed to deteriorate semiconducting properties. However, there have been no systematic studies on how these impurities are located in semiconductors and what electronic properties are produced by these impurities. The purpose of this project is to answer these questions, by using the first-principles calculation based on the density functional theory. In this report, we show some of the results.

We first consider what interaction is produced between impurity metal atoms when they are adsorbed on a molecule. This is because such interaction is essentially important to understand the preference of metal-atom clustering. Figure 1(a) shows the calculated interaction energy between two metal atoms (Al or Au) adsorbed on a pentacene molecule as a function of the metal-atom distance. It is seen that the energy is negative independent of the distance, which indicates that metal atoms prefer to adsorb on the same molecule and the inter-atom interaction is basically attractive. This result is quite different from the cases of Al atoms on a polyacetylene and graphene reported in the last year, where Al atoms are ionized and the inter-atom interaction becomes repulsive. Such difference of interaction character originates from the dimensionality of a molecule. Since a polyacetylene molecule and a graphene sheet are one and two-dimensional systems, respectively, they have various dispersive bands around the band gap.



Fig.1. (a) Interaction energy between two metal atoms adsorbed on a pentacene molecule as a function of the inter-atom distance. (b) Density of electron occupied bonding state (left) and unoccupied anti-bonding state (right).

Therefore, by using various freedoms of electronic states in molecules, the adsorbed metal atoms produce the independent bonds to the molecules. On the other hand, because a pentacene molecule is zero-dimensional system, respective energy band is located separately. As a result, adsorbed metal atoms produce the bonds by the strong hybridization with a single electronic state of the molecule. In fact, when two Al atoms are adsorbed on a pentacene molecule, as shown in Fig.1(b), there appear the bonding and anti-bonding orbitals between two Al atoms with the help of the electronic state of a pentacene. In this way, the interaction between adsorbed metal atoms basically changes depending on the electronic structures of molecules, i.e., especially the dimensionality of



Fig.2. (a) Calculated interaction energy between a single metal atom and two metal atoms adsorbed on graphene sheet as a function of the inter-atom distance. (b) Schematic picture of the most stable atom configuration.

molecules as a medium.

As seen in Fig.1(a), the interaction energy gain becomes the largest as the metal atoms are located nearby, which indicates that metal atoms prefer to produce a cluster. To confirm this feature, for example, we set three metal atoms on graphene sheet and study the interaction between two and one atoms, the result being shown in Fig.2(a). It is clearly seen that metal atoms prefer to combine as a single cluster. However, it is interesting to note that stable atom position changes from the center of hexagonal carbon ring in case of two atoms (Fig.2(a) inset) to the top of the ring in case of three atoms (Fig.2(b)). This occurs because the metallic bonding is first produced when more than three Al atoms are located nearby.

Finally, we consider how these metal-atom impurity changes the transport property of carriers. We adopt the Born approximation for the scattering of carriers by the impurity and calculate the hole carrier mobility based on the first-principles



Fig.3. (a) Calculated hole mobility of a pentacene solid as a function of impurity concentration in cases of Al and Au impurities. (b) Schematic picture of Al induced scattering potential in pentacene solid.

method, where the local potential difference (Fig.3(b)) is used as a perturbation. Figure 3(a) shows the hole mobility of pentacene thin film as a function of the impurity concentration, for cases of neutral Au and Al impurities. From this result, one can theoretically estimate the mobility of organic system by the first principles calculations for the first time.

These calculations were obtained using the TAPP and xTAPP codes developed by our consortium. In order to realize the calculations for organic systems, because the system is often made of a large number of atoms (more than 200 atoms), a large inter-molecule space, and a variety of molecular geometries, the advanced computing facility having higher-speed CPU more than 100G Flops, larger-size memory around 100GB, larger-size strange more than 1.0TB, and particularly a multi-task operation is indispensable. These conditions are never prepared in personal research laboratory. Only the present super-computing system of the ISSP can realize these calculations.

Theoretical analysis on the hydrogen-bonded conductor

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We have performed the computational analysis on the conductance of the novel hydrogenbonded material, catechol-fused ethylenedithiotetrathiafulvalene (H₂Cat-EDT-TTF). This material has been reported to show the significant conductivity compared with the other non H-bonding conductors [1]. Whereas the important contribution of the hydrogen nuclear quantum fluctuation in hydrogen bond has been expected, the detailed molecular mechanism of electronic conduction is still unclear. The understanding of such mechanism would be useful for the further development of the conducting material.

In order to elucidate the role of the hydrogen fluctuation in H-bond on the conductance, we calculated the dependency of the energy and the electrostatic properties on the position of the hydrogen atom in H-bond with some hydrogen bonded cluster models that were quarried out from the X-ray crystal structure. We found the significant change of the charge population upon the migration of the hydrogen atom, which expand to the neighbor molecular unit through the π - π stacking. According to the computational results, the significant intermolecular charge transfer coupled with the proton transfer was suggested [2].

We have a plan to perform the path integral molecular dynamics (PIMD) simulation to pursue how the thermal effect and nuclear quantum fluctuation of the hydrogen nuclei in H-bond will affect on the conductivity. The H/D isotope effect with PIMD simulation will be also carried out.

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Design of nanoscale carbon materials: Nearly free electron states of graphene nanoribbon under an electric field

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Recently, we have demonstrated that nearly free electron (NFE) states, which is inherent in the layered materials, are tunable by applying an external electric field normal to the atomic layers of these layered materials [1,2,3]. The NFE states of few-layered graphite shift downward under an external electric field and cross the Fermi level at a certain critical electric field that strongly depends on the thickness of the graphite thin films. Similar downward shifts have been also observed in h-BN thin films and transition metal dichalcogenide thin films, which exhibit electric field dependence similar to graphite thin films. In these cases, electrons are injected into NFE states under the critical electric field, which depends on both the thickness of the thin films and the constituent atom species of these materials. These downward shifts of the NFE state by the perpendicular electric field are ascribed to the potential gradient outside the films by the electric field that effectively leads to an attractive potential for the electronic states. In the present project, we aim to investigate the possibility of NFE state tuning by an electric field lateral to the graphene nanoribbons using

the first principles total energy calculation based on density functional theory with effective screening medium method.

We found that the NFE state appears not only in the vacuum region above the atomic layer of graphene, but also in the vacuum region outside the leftmost or rightmost atomic sites [4,5]. Furthermore, the NFE state substantially shifts downward with the application of a lateral electric field, and it eventually crosses the Fermi level, at which the nearly free electron carriers are injected outside We graphene nanoribbons. the also demonstrated that the critical electric field for injecting electrons into the NFE state strongly depends on the width of the graphene nanoribbon. The present findings indicate the possibility of an unusual one-dimensional electron system outside and along the edge atomic site of graphene in a lateral electric field. Furthermore, the accumulated electrons may decrease the contact resistance between graphene and metal electrodes.



Fig. 1 NFE states appeared in the alongside of the graphene nanoribbons

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Development of first-principles electronic-structure and transport calculation method based on real-space finite-difference approach

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Silicon carbide (SiC) is attracted much attention due to its excellent physical properties, such as a high thermal conductivity, high breakdown strength, and large band gap. However, unlike Si MOSFETs, SiC MOSFETs suffer from unacceptably low carrier mobility. One of the origins for the low carrier mobility is the generation of large amount of interface defects at SiC/SiO₂ interface during dry oxidation process. The understanding and precise control of the atomic structure of SiC/SiO_2 interface is necessary to increase the carrier mobility of SiC MOSFETs. In this project, density functional theory (DFT) calculations for the oxidation process of 4H-SiC(0001) surfaces and $4H-SiC(0001)/SiO_2$ interfaces for examining the initial and middle stage of oxidations, respectively, are conducted.

The DFT calculations are performed using the real-space finite-difference approach[1]. The details of calculation are introduced in Ref. 2. We first calculate the oxidation energies of the surface assuming the initial stage of the oxidation. The oxidation energies are computed by sequentially inserting O atoms between Si-C bonds around a particular C atom at 4H-SiC(0001) surfaces since the Si-O-C bonds are the most preferable structure except the drastic rearrangement of the bonding network at the interface. The typical computational models for the oxidation of 4H-SiC(0001) surface are illustrated in Fig. 1. The oxidation energy for inserting an O atom be-

tween Si-C bonds at the surface, E_n^{ox} , is determined by $E_n^{ox} = E_{(n-1)O} + \mu_O - E_{nO}$, where n is the number of inserted O atoms, E_{nO} is the total energy of the system with nO atoms, and μ_O is chemical potential of an O atom calculated by the total energy of O_2 molecule. We show in Fig. 2 the oxidation energy of the SiC surface with respect to n by white bars. For investigation of the C removal mechanism, C atom is taken from each model as a form of CO or CO_2 molecule. The possible sets of C and O atoms are removed from the oxidized surface and the most stable configuration are obtained. The energy gain of the emission from the system with nO atoms, $E_n^{(CO_x)}$, is determined by $E_n^{CO_x} = E_{nO}^{w/C} - E_{(n-x)O}^{w/oC} + E_{CO_x}^{total}$, where $E_{nO}^{w/C}$, $E_{(n-x)O}^{w/oC}$, and $E_{CO_x}^{total}$ are the total energies of the system with nO atoms, that with (n-x)O atoms without one C atom, and the total energy of the CO_x molecule, respectively. The calculated energies of the CO and CO_2 emissions with respect to *n* are shown in Fig. 2(a) by gray and black bars, respectively. CO_2 molecules are found to be the most preferable species at the initial stage of the oxidation.

We then examine the oxidation of a 4H- $SiC(0001)/SiO_2$ interface as a middle stage of the oxidation. Figures 1(d), 1(e) and 1(f) show the typical interface atomic structures during the oxidation. Figure 3 shows the calculated oxidation energies of the SiC/SiO₂ interfaces defined by the same procedure of the initial



Figure 1: 4H-SiC(0001) surface models of (a) n=2, (b) n=4, (c) n=4 after CO₂ emission. 4H-SiC(0001)/ β -tridymite SiO₂ interface model. (d) n=2, (e) n=3, and (f) n=3 after CO emission. Large dark gray, small dark gray, and light gray balls are C, O, and Si atoms, respectively. Reprinted from Ref. 2.



Figure 2: Oxidation energies (white bars) and formation energies of CO emission (gray bars) and CO₂ emission (black bars) at (a) SiC surface and (b) SiC/SiO₂ interface for different numbers of inserted O atoms, n. Reprinted from Ref. 2.

oxidation. Then the C emission from the interface is investigated. The energy gains due to the CO and CO_2 emissions are shown in Fig. 2(b). CO emission is preferred at n=3 because of the absence of the Si dangling bonds and Si-O-C bonds after the emission (see Fig. 1(f)). On the other hand, CO_2 emission is not the most preferable. This is because the inserted O atoms are preferentially consumed to form SiO_2 unit than CO_2 molecule. It is intuitive that the insertion of oxygen atoms increases volume. The CO emission at n=3 and the CO₂ emission at n=4 generate perfect SiO₂ networks containing neither dangling bonds nor Si-O-C bonds. In the case of the surface, the increase of volume due to the insertion of O atoms can be released in the direction perpendicular to the surface owing to the absence of SiO_2 , which results in the negative energy gain of the CO emission. On the other hand, the presence of SiO_2 prevents the increase of volume in the case of the interface. Therefore, CO molecules are emitted so as to reduce the volume of SiC substrate at n=3. Our results indicate that the formation of the interfaces is affected by the interface stress due to the lattice constant mismatch between 4H-SiC(0001)and SiO_2 . It is known that the electronic structure of the interface fabricated by the thermal oxidation shows different characteristics from that formed by the oxide deposition. The interface stress causes this difference in the electronic structure during the thermal oxidation.

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First-Principles Molecular-Dynamics Study of Structural and Electronic Properties of Covalent Liquids under Pressure

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To clarify the microscopic mechanism of changes in the structural and dynamic properties of amorphous or liquid covalent materials under pressure, we have carried out first-principles molecular-dynamics simulations [1-3]. To investigate the pressure dependence of the static structure, we obtain the structure factors, the pair distribution functions, and the distribution of the coordination numbers as a function of pressure. The bond-overlap populations and the Mulliken charges as well as the electronic density of states show the change in the covalent character in the materials due to compression.

From the simulations for amorphous silica, we found that a qualitative change occurs between 10 and 15 GPa in the pressure dependence of the static structure factor at ambient temperature. Up to 10 GPa, each Si atom is connected to four O atoms, and each O atom to two Si atoms. Reflecting the fact that the density becomes larger, the peaks in the bond-angle distributions shift to smaller angles. When the pressure reaches 15 GPa, Si atoms five-fold coordinated to O atoms appear, and also O atoms three-fold coordinated to Si atoms lower angles to form high asymmetry profiles. Si atoms six-fold coordinated to O atoms appear at 20 GPa, while four-fold coordinated O atoms exist at higher pressures over 40 GPa. Most of Si atoms have six-fold coordination, and the bond-angle distributions have new peaks at 40 GPa. We will study the pressure and temperature dependence of the transition to the permanent high-density structure by decreasing the pressure to ambient.

The local structure of amorphous and liquid germanium telluride mixtures has been also investigated. The calculated static structure factors are in good agreement with the experimental results. We confirmed that the shorter and longer bonds exist in amorphous GeTe as in the crystalline phase. It is known that crystalline GeTe has a rhombohedral A7 structure, distorted from rocksalt, where Ge and Te atoms are threefold-coordinated to Te and Ge atoms, respectively. However, a large fluctuation of atomic configurations was found, i.e., bond exchange between shorter and longer bonds occurs in amorphous GeTe. In the liquid phase, Ge atoms diffuse faster than Te atoms, and the Ge-Ge homo-polar bonds play crucial role for the larger diffusion coefficient.

First-principles study of quantum transport in nanostructures

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1 Introduction

The aim of this project is to reveal charge and heat transport in materials using atomistic theory. Quantum nature is essential in nanoscale systems, and atomistic analysis based on detailed electronic states calculations are indispensable to discuss the transport property. In order to analyze transport properties, we have developed the nonequilibrium Green's function (NEGF) method, and the time dependent wave-packet diffusion (TD-WPD) method. Using these methods, we have investigated charge and heat transport properties of atomic wires, organic molecules and so on.

2 Charge Transport

We have developed an efficient numerical calculation code for the ab-initio electron transport based on the DFT and NEGF formalism using Fortran and Message Passing Interface(MPI). The parallel computation technique with MPI is employed for efficient computations of density matrix via the the Green's functions, which depend on the energy and two-dimensional wave vectors. Since each matrix element of the Green's functions depends only on the single energy and two-dimensional wave vector point, it is possible to divide the calculations in the energy and wave vectors, which are carried out separately in each process. As a demonstration of the efficiency of the present code, the numerical calculations of electron transport properties of Al(100)-Si(100)-Al(100) heterostructures are shown in Fig.1. The computational efficiency is seen to



Figure 1: Speed-up ratio of total elapsed time by the parallelization of MPI in the ab-initio electron transport calculations in System B.

improve as the total number of processes becomes larger with the latency by the communication between whole process negligible. For an application, electron transport properties such as transmission spectra and total density of states are investigated for the systems with different thicknesses of Si layers. [1]

3 Heat Transport

Atomistic calculations of phonon transport properties have been performed using ab initio calculations and the nonequilibrium Green 's function method. The dynamical matrix is calculated on the basis of the density functional theory, and the transmission function is obtained using the Green & function, which is useful for the analysis of atomic-scale structures and the inclusion of quantum effects. Furthermore, phonon lifetime due to the phonon-



Figure 2: Computing time (red circles) and memory usage (blue triangles) per one initial wave packet as a function of site number of the lattice.

phonon scatterings by the anharmonic terms of interatomic forces is elucidated from atomistic levels. [2]

4 O(N) Method

We have also developed the O(N) TD-WPD method for the quantum transport calculation of huge systems of up to 100 million atoms. We calculated the conductance and the mobility of the system with micron-order lengths at room temperature based on the Kubo-Greenwood Using this method we can study formula. the transport properties from diffusive to ballistic regimes including the effect of realistic electron-phonon scattering, and determine the mean free path and relaxation time from an atomistic viewpoint. We performed DFT calculations of electronic structures and interactions between molecules of pentacene and rubrene single-crystal organic semiconductors including the effect of the van der Waals interaction, and applied the TD-WPD method to the analysis of transport properties of the organic semiconductors.

Based on the TD-WPD method, we have developed a methodology to evaluate the Hall effects of large-scale systems. We first apply the present method to the two-dimensional square lattice with the Anderson-type static disorder and confirm appropriate magnetic-field dependence of conductivities from the classical (weak magnetic field) to quantum (strong magnetic (a) Rubrene



Figure 3: (a)Molecular packing structure of rubrene organic semiconductor single crystal. (b)Temperature dependence of conductivities σ_{xx} , σ_{yy} , and σ_{xy} .

field) Hall effect regimes. Furthermore, we extend the method to take the microscopic molecular vibration effects into account and evaluate the influence of dynamical disorder on the Hall effects of organic semiconductors. [3]

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Analysis of hydrogen and oxygen reactions on solid surface/interface

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Understanding reactions on surfaces and interfaces is important for developing advanced materials and technologies. Various interesting physical and chemical phenomena are discovered at surfaces and interfaces, ranging from fundamental phenomena like tunneling effects to applications like catalytic reactions and migration of oxygen. This fiscal year, we have conducted various kinds of studies related to surfaces and interfaces [1], in different research areas. Highlights from our recent works include clean energy related issues, such as in photocatalysis [2] and several types of fuel cells, e.g., solid oxide fuel cell (SOFC), polymer electrolyte fuel cell (PEFC), or direct borohydride fuel cell (DBFC) [3, 4, 5, 6]. For diesel engine exhaust catalyst, we have widely investigated platinum based nanoparticles with different host/core materials using 3d-transition metals, wherein the activation of NO oxidation is determined [7, 8]. Due to the availability of the powerful and useful ISSP computational facilities, it has been possible for us to investigate various interesting and complex problems which can be difficult to deal with experimentally. In this report, we focus on the particular subject, i.e., surface of alloy materials, for instance Cu3Au. The composition ratio of these kind of materials at the surface layer usually differs from the bulk. This phenomena is called surface segregation. Surface segregation varies depending on the surface environment, e.g., oxygen pressure. To clarify these phenomena, we investigated the surface energies of different surface compositions with the aid of first principles calculations [9, 10]. In the clean surfaces, Au atoms tend to deposit on the first layer. The amount of Au atoms is highest in the (110) facet, 50 %-Au in (100)and (111) facets, and 75 %-Au in (110) facet. The (110) surface has the highest Au concentration among three facets because (110) surface is an open surface and has enough space for Au atoms which is relatively large atomic radius compared to Cu atoms. For an alloy surface in an oxygen environment, the oxygen atoms are adsorbed on the hollow site on the (100) and (111) facets, and at the long-bridge site on (110) facet. With increasing oxygen coverage, Cu atom concentration at the first layer becomes higher and reaches 100 % at 0.50ML of oxygen for all facets considered. These results are well agreeing with experiments. We further investigated oxygen atom penetration into the subsurface. We found that the activation barrier is quite higher on the segregated surface in comparison with pure Cu surfaces for all cases. This indicates that alloying of Cu with Au prevent oxidation of the material through surface segregation. The knowledge obtained in this study will help problems related to degradation of materials encountered in industry.

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First principles calculations on electronic structures and magnetism in transition-metal films and organic metal complexes

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Giant perpendicular magnetocrystalline anisotropy [1] — Much interest in 3dtransition-metal thin films with a perpendicular magnetic easy axis (PMCA) for the MgO-based magnetic tunnel junction has increased in nonvolatile spin-electronics. We here proposed a giant PMCA, up to 3 meV of $E_{\rm MCA}$, in a 7-layer Fe-Ni film/MgO(001), where an Fe₂/Ni/Fe/Ni/Fe₂ atomic-layer alignment with a bcc-like-layer stacking and the Fe/MgO interfaces lead to the large PMCA. The PMCA was importantly found to overcome enough over the magnetic dipoledipole anisotropy that favors the in-plane magnetization even when the film thickness increases.

Electric-field-induced modification in Curie temperature [2] — The Electric-field (*E*-field) induced magnetism in 3*d* transition-metal thin films has shown promise as a potential approach offering a new pathway to control magnetism at the nano-scale with ultralow-energy power consumption. We here demonstrate an *E*-field-induced Curie temperature ($T_{\rm C}$) modification of a freestanding Fe monolayer and a Co monolayer on Pt(111). An applied *E*field is found to modify the magnon energy; the change arises from the *E*-field-induced screening charge density in the spin-spiral states due to p-d hybridizations. The Heisenberg exchange parameters obtained by the magnon energy suggest an E-field-induced modification of the $T_{\rm C}$, which is demonstrated via Monte Carlo simulations.

Electronic configurations and magnetism in organic-metal complexes [3] — In organometallic molecules, the electronic configuration of d electrons is an essential aspect in magnetic properties but it is often difficult to analyze it. Here, based on the constraint density functional theory, we systematically investigated for prototypical molecules of metallocenes, MCp₂. The results predict that the ground states for M=Cr, Mn, Fe, Co, and Ni are the ${}^{3}E_{2g}$, ${}^{2}E_{2g}$, ${}^{1}A_{1g}$, ${}^{2}E_{1g}$, and ${}^{3}A_{2g}$ states, respectively, and the magnetizations of the CoCp₂ and NiCp₂ energetically favor highly orienting along the perpendicular and parallel directions to the cyclopentadienyl plane.

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Theoretical Analyses on Electronic and Ionic Transport Properties of Nanostructures

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1 Introduction

Although the electrical properties of nanostructures have been extensively investigated in the last few decades, our understanding on them is still insufficient to design and control novel nanoscale electronic devices. In particular, further studies on complicated situations and phenomena, such as time-varying electronic transport and the interplay among electronic and ionic transport at nanoscale, are strongly desired.

Keeping the above in minds, we have been investigating these topics using theoretical analyses based on atomic/electronic level simulations. In the followings, some of our results in the fiscal year 2014 are described.

2 AC transport in nanostructures

Clarifying responses of nanostructures to AC signals is crucial for the realization of nextgeneration ultrafast devices. So we have been studying AC transport properties of metallic carbon nanotubes (m-CNTs). Recently, we have examined the AC transport properties of m-CNTs with randomly distributed impurities using the nonequilibrium Green's function method [1]. In doing so, we focus on the dependence of the transport behaviors on the impurity potential's range and amplitude and the impurity concentration.

We have found that the short-range impurity scattering causes a decrease in the emittance as well as the DC conductance. This behavior can be attributed to electron scattering [2]. On the other hand, we found that the long-range impurity scattering causes the emittance increase when the potential amplitude and/or impurity concentration increase. Considering the fact that the variation of this scattering does not alter the DC conductance, the above behavior is interesting. We have shown that the behavior can be understood from the change in the dwell time of electrons and their multiple scattering: The multiple scattering increases the dwell time, which in turn increases the kinetic inductance and thus also the emittance. Our results show that the electron scattering is important to understand the inductive response as well as the capacitive one.

3 Interface structures in tantalumoxide-based resistance switches

Resistance switching devices based on amorphous tantalum oxide $(a-TaO_x)$ have attracted attention as promising candidates of future memory devices. Aiming at the microscopic understanding on their switching behaviors, we had examined atomic structures of conductive filaments (CFs) in the oxide using the density functional theory (DFT) [3, 4]. Recently, we have examined the structures of the interfaces between the oxide and metal electrodes to get an insight into the initial process of the CF formation [5].

Models of a-TaO $_x$ were obtained using meltquenching process via first-principles molec-
ular dynamics. Then structure optimization and subsequent melt-quenching were performed for the heterostructures consisting of an a-TaO_x layer sandwiched between fixed Cu and Pt layers. Finally, the obtained Cu/a-TaO_x/Pt heterostructures were further equilibrated at room temperature and then optimized with the relaxation of all atoms. To examine the effect of interface O concentration, we adopted three models, Cu₁₀₈Ta₃₂O₈₀Pt₈₄, Cu₁₀₈Ta₃₂O₈₈Pt₈₄ and Cu₁₀₈Ta₃₂O₉₆Pt₈₄.

We have found that the O-rich Cu/TaO_x interface is stable within a wide range of O chemical potentials. At this interface, a considerable number of interface Cu atoms tend to migrate to the a-TaO_x layer, which causes the formation of the Cu₂O layer. The interface Cu atoms become more ionized with an increase in the interface O concentration and/or temperature. These ionized Cu⁺ ions could work as a main source for the formation of CFs in the Cu/a-TaO_x/Pt resistance switch. On the other hand, the Pt electrode is not ionized, irrespective of the interface O concentration and temperature.

4 Capacitance of charged bilayer graphene

Bilayer graphene (BLG) is promising as a channel material in the field effect transistor (FET) owing to the controllability of band gap by electric field. Recently, quantum capacitance of BLG was measured to get a clue for improving the performance of BLG-based FET [6], because the quantum capacitance is closely related to the density of states. However, it is difficult in experiments to distinguish the capacitance change due to the band structure change by the doping and/or applied field from the quantum capacitance. So we have calculated the dielectric properties, especially capacitance, of BLG using the DFT.

First, the electronic states of BLG have been calculated with applying an electric field but without doped charges. Local relative permittivity of BLG has been estimated from the calculated changes in electrostatic potential and charge distribution due to the applied field. The local relative permittivity is larger than two even in the middle of the two graphene layers, which suggests that the simple picture behind the capacitance consideration, two metallic electrodes, is not relevant in this case, and the BLG should be regarded as a single dielectric material.

Next, the electronic structures of BLG with doped charges under an applied electric field have been calculated by the effective screening medium method within the DFT. The results suggest that the energy required to modify the band structure of BLG is in the order of 10 meV, and thus the effect of the band structure change on the quantum capacitance measurement of BLG is negligible. In addition, we find that the band gap is weakly dependent on the amount of doping, besides being dependent on the applied electric field.

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Ab initio study of thermoelectric properties of molecules between magnetic electrodes

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The molecular junction is a promising system to achieve maximum thermoelectric efficiency due to the quantum confinement of the molecular orbital (MO) into the nanoscale gap [1]. We propose to use molecular junctions with ferromagnetic electrodes as it can induce the spin polarization of MOs and then tune the Seebeck coefficient. We investigate the transport properties of Ni-benzenedithiol (BDT) -Ni molecular junction with the nonequilibrium Green's function method based on density functional theory. Result revealed that one of the spin split highest occupied MO of BDT appears just above the Fermi level, indicating an increase in the magnitude of S (compared to when Au electrode was used) and a change in the sign as well. We obtained negative and large S for Ni-BDT-Ni junctions. We further investigated the effect of spin configuration of electrodes and surface roughness on S[2].

We also performed a computational research to confirm the possibility of a molecular resistive switch obtained via sliding multiple anchoring points. Our calculation revealed that the change in the effective wire length of the oligo-thiophene between Au electrodes explains the three conductance values obtained in the experiment.

The structural optimization performed with the SIESTA program [3] on System B was very helpful to advance our research works.



Figure 1: Sign change of the Seebeck coefficient due to the spin-splitting at the Ni-BDT-Ni junction.

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First-principles molecular dynamics simulation of the water/surfactant interfaces

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The sum-frequency generation (SFG) spectroscopy is a powerful tool to study the structure and dynamics of interfacial molecule, because molecules in a few nm regions at surfaces or interfaces give SFG signals. Since the SFG signals are often complex reflecting the inhomogeneous environment of interfaces, all-atom simulations are useful for the interpretation. The classical molecular dynamics (MD) simulation based on the force field model is usually used to simulate the SFG signal. However, delocalized electronics states of the solid surfaces are difficult to be described by force-field models.

Ab initio MD (AIMD) is a powerful tool to describe heterogeneous systems such as the water/solid interface, Although AIMD is computationally too expensive to calculate the SFG signal. We developed a surface-specific velocity-velocity autocorrelation function, relating to the SFG spectroscopy. By using this function, converged SFG signals can be obtained from ~100 ps trajectory, which is an order of magnitude shorter than the conventional dipole-polarizability time correlation function. First of all, the SFG spectrum of the water/air interface calculated from AIMD trajectory should be checked. We accumulated 160 ps trajectories by using the CP2K code [1] and revealed that the SFG signal reproduces the most of the features found in experiments [2].



Fig. 1: SFG response function of water OH stretch mode represented by velocity-velocity autocorrelation function.

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Ab-initio study of organic semiconductor thin film growth

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Organic semiconductors have attracted considerable interest because of their favorable electrical properties for development of organic electronic devices. Among them, Pentacene (Pen) is an important organic-semiconductor material because of its high carrier mobility characteristic when it applies to the thin-film transistors. It is well known that the matching of the work function of the electrode layer with the energy level of organic semiconductors is crucial to inject carriers effectively. However, conventional electrode such as Al has poor electrical conduct with Pen due to their mismatching. Recently, graphene has attracted much attention in the application for transistors, light-emitting diodes, and solar cells.[1, 2] In addition, it is particularly suited for implementing transplant electrode in organic devices. Acceleration of the carrier mobility has also been tried by forming Pen layers on a graphene electrode. Because both the frameworks of Pen and graphene consist of carbon atoms, the best energy matching between the electrode and the organic molecule can be expected. Surprisingly, electronic property at the interface between the graphene electrode and the organic semiconductors is not well known. In this work, we performed large scale van der Waals density functional electronic structure calculations (vdW-DFT) to investigate the detailed electronic structure at the interface. The results are compered to those of the Grimm's D2 calculation (DFT-D2) where the vdW interaction force is empirically implemented in

the DFT. The standard DFT calculations with the local density approximation (LDA) and with the generalized gradient approximation (GGA/PW91) are also performed for verification.



Figure 1: Pentacene on graphene. Bright (yellow) part is the increased charge density region as a result of the adhesion.

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Computer Simulations of the Barkhausen Effects

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Relating with the last year investigations of the nano-materials magnetizations, the Barkhausen effects caused by the magnetic dipole moment interactions in Fe metal are cleared in this work. Using the ISSP system A (shii), the Fortran programs of the nano-Fe magnetizations are executed by about 500 line programing compiled with sxf90. The used times are about 18 hours par job using p4system for drawing the domain structures, the magnetization curves and the Barkhausen effects.

The magnetic systems of spins are generally calculated using the Hamiltonian

$$\hat{H} = \sum_{i \le j} J_{ij} \hat{\boldsymbol{\mu}}_i \cdot \hat{\boldsymbol{\mu}}_j + \sum_{i \le j} W_{ij} + \sum_j \boldsymbol{\mu}_j \cdot \boldsymbol{H}, \qquad (1)$$

where the first term is the electronic binding energy with spin-spin interactions, the second term is the dipole moment interactions of spins and the third term is magnetization energy in the external field **H**. The electronic binding energies of 3d electrons in Fe are induced from the tight binding interactions of the directed magnetic moments bounded by the Hunts rule. These 3d and 4s electrons construct the eigenstates in the external field environments. In this situation, the quantum states take the same reversible states at the same external field H. These states trace only the one line magnetization curve without irreversible Thus. hysteresis curves. many-many investigations using the Hamiltonian without the second term cannot explain the Fe hysteresis curves. The realistic magnetization curves are produced by the Hamiltonian (1) including the three terms.

In this paper, only the Hamiltonian composed of the second and the third terms are calculated for only clearing the hysteresis characteristics. Setting distance vector $d_{ij}=e_{ij}d_{ij}$ between dipole moments at *i* and *j*, the interaction energies are equated as

$$W_{ij} = \frac{1}{4\pi\mu_0 d_{ij}^3} \{ (\boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j) - 3(\boldsymbol{\mu}_i \cdot \boldsymbol{e}_{ij})(\boldsymbol{\mu}_j \cdot \boldsymbol{e}_{ij}) \}$$
(2)

In simulations of Fig.2 and Fig. 3, the magnetic moments are set to have freedoms of



Fig. 1. Two magnetic moment interactions. The dipole moments are equated as $\mu_i = n_b \mu_B^0 = \delta_i \Delta \psi$



Fig. 2 Magnetization curve $(B_m=n_b)$ in a *NxNyNz*= $20 \times 4 \times 40$ lattice point system. The aria A is precisely calculated and drawn in Fig. 3 to show the B effects.



Fig. 3 The terraces ΔH_B and the jumps ΔM_B of the B effects in the precise magnetization curve at the aria A in Fig.2. The coercivity becomes $\mu_0 H_c = 0.0456$ T, which coincide with the experimental data.

26 directions.^{[1][2]} The precise structures at the jump points of a circle in Fig. 2 are drawn in Fig. 3. Crystal Fe takes the BCC structure with the lattice constant $a=2.86\times10^{-10}$ [m] up to 911 °C and have the dipole moments of $2n_b\mu_0\mu_B$ per a lattice. The constants are $n_b=2.22$, permeability μ_0 and the Bohr magneton μ_B respectively. Through these results, the processes of the Barkhausen effects are clarified as the transitions of the dipole-moment arrangements in the magnetic domains.

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Coadsorbate-Induced Energy Shifts of Ferrocene Derivatives Adsorbed on Au(111) Electrode

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A microscopic understanding of electrochemical properties is of fundamental importance for future electrochemistry. The assessment of the energy cost to remove an electron from molecules adsorbed on metal electrodes is essential for many applications. Using ferrocene terminated monolayers (Fc SAMs) on Au(111) electrodes, we have recently revealed a linear relation with a slope of ~ 0.7 between the highest occupied molecular orbital (HOMO) and the electrochemical formal potential [1], but its microscopic origin is not clear at this stage. In this study, we calculated electronic properties of the Fc SAMs and compared to experimental formal potentials.

Structural optimization and electronic property calculations were performed using the program "STATE". Fig. 1 shows our Fc SAM systems. A Fc-terminated molecule was coadsorbed with three 1-butanethiol (Fc_Me) or 4-mercapto-1-butanol (Fc_OH). Their work function and energy of Fc backbone were calculated by usual methods.

The obtained values are summarized in Table 1. Work functions of the systems were consistent with the direction of dipole moment of the coadsorbed molecules. HOMO energies were found to be shifted deeper with the decrease of the work functions. This indicated that the Fc backbone of the Fc_OH system is more difficult to transfer an electron to the electrode Fermi level compared to that of the Fc_Me system, in contrast to the expectation from the experimental formal potentials [2]. These results indicate the importance of solvation energy, which is our next target.



Fig. 1: Optimized structures of Fc SAMs.

Table 1: Electronic properties of two systems.

	Fc_Me	Fc_OH
Work function (eV)	3.81	3.41
HOMO energy (eV vs $E_{\rm F}$)	-0.53	-0.80
Formal potential (V) Expl.	+0.40	+0.27

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Study on physical and structural properties of defects, surfaces, and interfaces for 2D semiconductors

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Two dimensional (2D) semiconductors such as graphene, h-BN, and transition metal dichalcogenide show very unique physical properties. In our project, we focus on the physical and structural properties of defects, surfaces and interfaces of them.

h-BN is expected as a high-quality supporting substrate for graphene. h-BN substrate rarely produces electron-hole puddles in graphene. h-BN is also expected as a highquality gate insulator because of its wide band gap and atomic thickness. In both cases, h-BN must be uniform and free from any defects. However, the experiments based on TEM observe large holes in h-BN [1]. These holes are thought to be generated by the charging effect due to the electron beam injected by the TEM. Okada approached this phenomena theoretically based on the first-principles calculation [2]. We have extended his theoretical study and investigated larger holes such as V_{B6N3} and V_{B3N6} (Fig. 1). We use the firstprinciples calculation program PHASE [3] on System B for the purpose.

The obtained formation energies show that the larger holes are stabilized in the higher electronic chemical potential condition (Fig. 1). This suggests that accumulation of negative charge can induce larger holes in h-BN sheets. Further studies in detail of the electronic and structural properties of the h-BN holes are now in progress.



Figure 1: Formation energies of various holes as the function of the electronic chemical potential in the B-rich condition. Atomic structures of the holes V_{B6N3} and V_{B3N6} are also shown in the bottom.

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Development of *ab initio* GW plus cumulant code

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Using *ab initio* GW and its cumulant expansion method, we study quantitative accuracy of plasmaron states of various materials. The plasmaron state is a coupled state of free electron and plasmon, and can be observed in a metallic system, especially having isolated low-energy bands near the Fermi level. In the isolated-band materials, the plasma excitation can occur in this band, and then its energy scale is usually smaller than the bandwidth. In this case, the plasmon excitation can renormalize the bare band structure via the self-energy effect and generate a coupled state of free electron and plasmon.

In this report, we present a study for the low-energy plasmaron state of transition-metal oxide $SrVO_3$ which is a typical isolated lowenergy band system. This is widely known as a correlated material, but in this study, we investigate another point of view of the plasmon excitation. In fact, for this material, the lowenergy plasmon excitation is experimentally observed in reflectance and electron energy loss spectroscopy (1.4 eV). The bandwidth estimated by density-functional calculations is 2.7 eV, and thus, the plasmon-excitation energy are smaller than the bandwidth. Therefore, it will be interesting to calculate the self-energy effect due to the plasmon excitation with the GW calculations. As is well appreciated, the GW calculation gives a good estimate for the quasi-particle energies, while it is less accurate for the satellite feature concerned with the plasmaron state of electronic structure.

To this end, we have extend our developed GW code to its cumulant-expansion one, which

is based on the plane wave basis set with the pseudopotential approximation. With these codes, we calculate the spectral function to see the formation of the plasmaron state, and compare the GW and the cumulant-expansion results. The code is massively parallelized, capable to treat huge systems such as organic compounds. All calculations were done at Supercomputer center at Institute for Solid State Physics, University of Tokyo.

Figure 1(a) is our calculated reflectance (curve) as a function of frequency of $SrVO_3$. The drop from 1 to 0 specifies the plasma frequency and the value is 1.8 eV. We found that our spectra well reproduce the experimental one such as a 1.4-eV drop (dots).

Figure 2 is the GW spectral function of $SrVO_3$, in which we display the region including oxygen-*p* band, as well as vanadium t_{2g} band. The density-functional bands are drawn by solid curve. The bright regions around 11 eV at the *R* point and 5 eV at the Γ point indicate the formation of the plasmaron states. Figure 3 is the GW plus cumulant-expansion result. We see that the weights due to the plasmaron states become somewhat large and lower toward the Fermi level.

Finally, we compare the photoemission results among GW plus cumulant (thick curve), GW (dashed curve), density-functional theory (thin curve), and experiments (dots) of SrVO₃. Within the displayed energy range, the GW and GW plus cumulant results are similar and are in a reasonable agreement with the experimental results.

In summary, we have studied low-energy



Figure 1: Comparison of reflectance between theory (curve) and experiments (dots) of SrVO₃.



Figure 2: Calculated GW spectral function $A(\mathbf{k}, \omega)$. Red curves are the density-functional results and the Fermi level is 8.15 eV.

plasmon excitations of transition-metal oxide $SrVO_3$. To investigate the quantum accuracy of the plasmaron state, we have developed the GW plus cumulant-expansion method, and compared its electronic structure with the usual GW result and experiments.

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Figure 3: Calculated GW plus cumulantexpansion spectral function $A(\mathbf{k}, \omega)$.



Figure 4: Comparison of photoemission spectra among GW plus cumulant (thick curve), GW (dashed curve), density-functional theory (thin curve), and experiments (dots) of SrVO₃.

Ab-initio study of thermoelectric effect in ferroelectric BaTiO₃

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By means of density-functional calculation and Wannier function method, Seebeck coefficients are calculated for *n*-type BaTiO₃ at the first time. It turns out that the polar structural distortion of Ti and O ions leads to the peculiar band dispersion of the lowest conduction Ti- t_{2g} band, which enhances the Seebeck coefficients along the polar axis.

Since the finding of large Seebeck coefficients for NaxCoO₂, transition-metal oxides have emerged as one category of thermoelectrics. Electron-doped SrTiO₃ and KTaO₃ have been found to have the large Seebeck coefficients S, which are comparable to that of Bi₂Te₃, while also having the metallic conductivity σ . Several density functional theory (DFT) calculations have been performed on such hermoelectric transition-metal oxides, which have mostly concluded that narrow t_{2g} bands with the anisotropic mass m^* are responsible for the large Seebeck coefficients.[1]

In this study, we make use of the ferroelectric distortion in BaTiO₃ in order to enhance the anisotropy of the m^* of Ti- t_{2g} electrons, which leads to the increase in the Seebeck coefficients. We performed DFT calculations using the VASP code with GGA-PBE potential. To calculate the band velocity, the Wannier function approach implemented in the BoltzWann code was employed. System B cluster system was mainly used for the computation. Our results show that the calculated Seebeck coefficients in BaTiO₃ is anisotropic as having low S_{xx} and high S_{zz} , the latter is superior than the S in SrTiO₃. The increase in S_{zz} originates from a single-band contribution from the Ti- d_{xy} band, which shows an isoenergy surface elongated along the k_z direction. The polar structural distortion lifts the three-fold degeneracy in Ti- t_{2a} bands, which in turn causes the strong anisotropy in the electron velocity. In this peculiar situation, the Seebeck coefficients are highly increased. Using the unique property, it might be possible to control the thermoelectric performance by using the piezoelectric effect. When uniaxial strain is applied on $BaTiO_3$ crystal, both the polar axis and the thermoelectrically favored direction could be manipulated as wished. This effect requires to be confirmed by future theoretical and experimental studies. More detail results and discussions can be found in a reference.[2]

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First-Principles Calculation of Transition-Metal Compounds

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A first-principles density-functional-theory method has been applied to various condensed matter and surface systems for the last few decades. In this project, we study the electronic properties of several transition-metal compounds, especially oxide systems, and explore their chemical trends and effects associated with crystal structure and symmetry. In addition, continuing developments of numerical methods related to the first-principles calculations are also pursued. In FY2014, we focused on first-principles study of the electronic structure of A-site ordered perovskitetype transition-metal oxides.

Among the known A-site ordered perovskite oxides, we have investigated the electronic structure and magnetism of CaCu₃Fe₄O₁₂ (CCFO) [1] and $CaCu_3B_4O_{12}$ (B=Ti, Ge, Zr, and Sn) [2] in the previous projects. Related to these oxides, the electronic structure of $LaCu_3Fe_4O_{12}$ (LCFO) is investigated by means of first-principles calculations [3]. LCFO reveals metal-to-insulator and paramegnetic-to-antiferromagnetic transitions with a volume expansion by 1.3% at 393K as temperature decreases. This is believed to be associated with a charge transfer as $3Cu^{2+}+4Fe^{3.75+} \rightarrow 3Cu^{3+}+4Fe^{3+}$, according to a bond distance analysis. This is remarkably contrastive to the charge disproportionation as $4Fe^{4+} \rightarrow 2Fe^{3+}+2Fe^{5+}$ seen in CCFO. In LCFO the electronic structure changes from insulating to metallic as the Cu valence shifts from nonmagnetic Cu^{3+} to spinpolarized Cu^{2+} at the transition. This type of transition may occur by pressure as shown in Fig. 1, being consistent with experiments. The stability of the high-pressure phase is actually realized by the valence change of Cu^{3+} to Cu^{2+} and accordingly, a ferrimagnetic (FiM) phase is stabilized because of dominant anti-



Figure 1: Calculated total energies of $LaCu_3Fe_4O_{12}$ as a function of unitcell volume in antiferromagnetic (AFM) and ferrimagnetic (FiM) phases shown by dots and solid squares, respectively.

parallel magnetic couplings between Cu and Fe ions. Therefore, it is natural to consider the observed high-temperature phase is a paramagnetic phase associated with the FiM phase. We found that the volume change at the transitions is a key for understanding the changes in the electronic structure and magnetism.

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Density functional theory study of stability and dynamics of metal nanoclusters on a silicon surface

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Small atomic clusters have attracted much attention, owing to their intriguing physical properties, and to the great potential as components of future microelectronics devices, high density storage devices, and catalysts. Recent progress in scanning probe microscopy enable one to manipulate atoms and molecules one by one, and it is becoming possible to fabricate well defined small atomic clusters on surfaces. Although the precise control of the number of constituent atoms in the cluster is possible, it is difficult to determine the atomic structures only from the experiment, and the atomistic simulation plays an important role to understand the atomic as well as electronic structures of clusters. In this work, I perform density functional theory calculations of Pb₃ on $Si(111)(7 \times 7)$, to clarify the atomic structures of the Pb_n clusters, and the mechanism of the atomic switching realized by the scanning tunneling microscopy (STM).

All the calculations were performed using the STATE[1] code. We used a plane-wave basis set to expand the wave functions and ultrasoft pseudo potentials to describe electronion interactions. The surface was modeled by a slab composed of eight atomic layers, and a thick enough vacuum was inserted between the neighboring slabs. The effective screening medium method[2] was used to eliminate spurious electrostatic interactions with the image slabs.

I have examined several configurations of Pb_3 on $Si(111)(7 \times 7)$ and found that none

of them can reproduce the polarity dependent STM topography. This motivated me to consider the structures including Pb substitutions, because experimentally a single Pb atom replaces a substrate Si adatom at a few 100 °C and the contrast pattern strongly depends on the bias. By examining several cluster models with Pb substitutions, I have arrived at a structure, which nicely reproduces the observed filled and empty state STM images. Thus, the Pb_3 is no longer a singleelement cluster, but a binary cluster composed of Pb and Si atoms. Furthermore, it is proposed that the atomic switching induced by STM is caused by the formation of a single electron/hole, which strongly couples to the atomic motion. However, switching involves the complicated reaction pathway of the concerted atomic process, and further effort is required to understand its detailed mechanism.

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Hybrid *ab initio* QM/MM calculations of biological macromolecules

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theoretically investigate То functional mechanisms of biological macromolecular systems, we employed ab initio quantum mechanics (QM) calculations, coupling to molecular mechanics (MM) calculations for the systems involving the entire structures. In the hybrid QM/MM calculations, we used our interface program, which connects highlyparallelized engines for the QM and MM calculations. In this study, we analyzed the interactions between the catalytic center of an the ligands, elucidate enzyme and to molecular mechanisms involving the recognition in the biological system based on the electronic structures of the reaction center.

Cytochrome c oxidase (CcO), which is the terminal enzyme of the electron transfer system from a biological point of views, reduces an oxygen molecule (O₂) to two water molecules (i.e., $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$). The catalytic reaction produces the free energy, which is utilized for the proton pump activity of CcO, generating the gradient of the proton concentrations between mitochondrial membranes.

The catalytic reaction center of CcO is composed of so called the Cu_B site and heme a_3 , including transition metals, i.e., Cu and Fe ions, respectively (**Fig. 1**). Thus, the reaction center is referred to as the binuclear center (BNC). The binding of oxygen to the BNC is a trigger of the catalysis. However, from an experimental point of views, various ligands, such as CO, NO, and CN, have been employed to investigate the three-dimensional (3D) structures of the ligandbound forms of CcO (this is because it is impossible to obtain a stable structure in the complex with the reactive molecule).

Thus, our aim is to investigate the interaction mechanisms between the ligand oxygen molecule and the BNC, thereby approaching to the catalytic mechanisms of CcO. Still, it is not always so easy even to definitely identify the correct configurations of the (inactive) ligands that are bound to the transition metals in the BNC. Thus, the interaction modes between the BNC and the (inactive) ligands are still left to be clarified.

To identify the optimal configurations of CO and the BNC, we calculated the interaction energy values between the ligand and the Cu_B site of bovine CcO, by putting the ligand molecule to various positions (500 configurations for each case) in the vicinity of the BNC. Here, we employed the UB3LYP functional and the TZVP basis set for the transition atoms and the coordinated atoms. Also, we examined advanced functionals, such as M06X, for the comparison.

Our systematic energy mapping analysis revealed that the appropriate CO configurations are dispersed as a spheroid in the vicinity of the Cu ion. In fact, this is consistent with the electron density that was observed in the crystallographic data. Furthermore, we found that at least the two "distinct" configurations exhibited a "small" energy difference (< 2 kcal/mol). In fact, the atomic distances between O atom of CO and Fe of heme a_3 are different, by as large as ~1Å, with respect to the two distinct types of the configurations.

To further examine the characteristic features in the ligand configurations, we calculated the IR spectrums, and found that the corresponding peaks fit well to the experimental values. Note here that the two configurations of CO are corresponding to the distinct IR peaks, thus indicating again that these configurations were involved in the (semi)stable interactions of the Cu_B and CO.

Moreover, we found that the Val243 side chain contacted the CO where the distance of O atom and the Fe of heme a_3 is closer, thereby producing the configuration that is distinct from another one. We further found that a previous biochemical mutagenesis study in terms of this Val residue also supported our data.

Note here that the above-mentioned modulation of the ligand configuration through the Val243 side chain led to the presence/ absence of hybridization between a *p*-orbital of the CO and a *d*-orbital of Fe in heme a_3 , thereby resulting in the two distinct vibrational modes of the CO stretching, which were corresponding to the previous spectroscopic data. Thus, we concluded that Val243 is a determinant for the configuration of CO interacting with the Cu_B site.

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Fig. 1. The catalytic reaction center of bovine cytochrome c oxidase (CcO) is depicted. The reaction site involves heme a_3 and the Cu_B site, thus referred to as the binuclear center (BNC). The Cu_B site and heme a_3 include Cu and Fe ions, resepctively. In the Cu_B site,

the three histidine (His) residues coordinate to Cu_B ion (for one His residue, Tyr244 is covalently-bonded), and a His residue coordinates to Fe ion from an axial direction in heme a_3 . In the right panel, Val243 (see text) is dipicted.

First-Principles Study on Charge-Discharge Reaction Mechanism in Cathode Materials of Secondary Batteries

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We have mainly used the supercomputer systems to investigate battery reaction mechanisms in cathode materials of Na-ion secondary batteries in the fiscal year 2014. In this project, first-principles calculations were done by using the HiLAPW code which is based on the density functional theory with the all-electron full-potential linearized augmented plane wave method. We have mainly studied microscopic reaction mechanisms in a solid Na/S battery system [1] and in the Na_xC₆O₆ organic cathode material [2]. This research was done in collaboration with Tamio Oguchi. We also contribute partly to clarify electronic properties of a perovskite oxide system [3].

Structural and electronic properties of α -S and Na-S crystals [1]

To understand microscopic mechanisms of charge and discharge reactions in lowtemperature Na/S batteries, there has been increasing needs to study fundamental atomic and electronic structures of elemental S as well as that of Na-S phases. The most stable form of S is known to be an orthorhombic α -S crystal at ambient temperature and pressure, and α -S consists of puckered S₈ rings which crystallize in space group Fddd.

In this study, the crystal structure of α -S is examined by using first-principles calculations with and without the van der Waals interaction corrections of Grimme's method, and results clearly show that the van der Waals interactions between the S₈ rings have crucial roles on cohesion of α -S. We also study structure stabilities of Na₂S, Na₂S₂, Na₂S₄, and Na₂S₅ phases with reported crystal structures. Using calculated total energies of the crystal structure models, we estimate discharge voltages as shown in Figure 1 assuming the four-step discharge reaction equations as

$$\begin{array}{rcl} 2\mathrm{Na} + \mathrm{S} & \rightarrow & 8/5\mathrm{Na} + 1/5\mathrm{Na}_2\mathrm{S}_5 \\ & \rightarrow & 3/2\mathrm{Na} + 1/4\mathrm{Na}_2\mathrm{S}_4 \\ & \rightarrow & \mathrm{Na} + 1/2\mathrm{Na}_2\mathrm{S}_2 \\ & \rightarrow & \mathrm{Na}_2\mathrm{S} \end{array}$$

estimated from the energy stability analyses. Calculated voltage-capacity characteristics in solid Na/S battery systems are discussed by comparing with recently reported experimental results.

Electronic and atomic structures of $Na_xC_6O_6$ organic cathode material [2]

Na-ion batteries have been explored as a promising alternative to Li-ion batteries owing to a significant advantage of a natural abundance of Na. Recently, it has been reported that disodium rhodizonate, $Na_2C_6O_6$ (Figure 2), exhibit good electrochemical properties and cycle performance as a minor-metal free organic cathode for Na-ion batteries. However, its crystal structures during discharge/charge cycle still remain unclear.

In this work, we theoretically propose feasible crystal structures of $Na_{2+x}C_6O_6$ depending on Na concentrations x using first-principles calculations. Structural phase transitions have been found: $Na_4C_6O_6$ has a different C_6O_6 packing arrangement from $Na_2C_6O_6$. Voltage values and electronic structures of $Na_{2+x}C_6O_6$ as a function of x are clarified and discussed comparing with the experimental results. Our theoretical findings could contribute to understand the microscopic discharge/charge reaction mechanisms of $Na_2C_6O_6$.



Figure 1: Calculated capacity-voltage curve of solid Na/S battery under the assumption of four-step discharge reaction equation.



Figure 2: Crystal structure of disodium rhodizonate $Na_2C_6O_6$.

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First-Principles Calculation of Transition Metal Oxides Interfaces

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Recently, the two-dimensional electron gas (2DEG) formed at the transition metal oxides interface has attracted much attention for applications in the next generation device. The perovskite heterostructure composed dielectric materials LaAlO₃/SrTiO₃ is one of such systems extensively studied. The polar interface induces large built-in electric field. Therefore, the electric-field induced spin-orbit interaction (SOI) in the perovskite heterostructure is quite important in understanding the electronic structures. In this research, by using large-scale first-principles calculations based on the density functional theory implemented OpenMX[1], , we revealed specific electronic states and properties formed at the interface of the transition metal oxides modeled by superlattice. We focused on how spins can be controlled by electric field (electric polarizations and charge carriers). In additions to the 2DEG in the oxides heterostructure, we also revealed that the effect of SOI in strained ZnO film, The applications of 2DEG at the oxide interface, we proposed anomalous Seebeck effect.

We have performed first-principles calculations of $(LaAlO_3)_n/(SrTiO_3)_n$ (n=2-8). We evaluated the spin-orbit coupling constant, the Rashba parameter, for the interface states. In addition, we investigated the spin textures, i.e., momentum vector dependent magnetic field in the Brillouin zone. We found electron doping in the TiO₂ layer at LaO interface and hole doping in the AlO₂ layer at SrO interface. Due to the built-in electric field at the interface, the interface states show spin splitting and vortex-like spin textures in momentum space, i.e. Rashba effect. Calculated Rashba coefficient is of the same order as that of the experimental value and theoretical value for n=2[2].

We also have perform first-principle calculations of wurtzite ZnO and thin-film surface system. We have performed large scale computation up to 120 ZnO bilayer and the period of unitcell is about 20 nm. We evaluated the spin texture whose energy is slightly higher than that of the conduction band bottom in the surface banbs in nonpolar surface. We find that in-plane electric polarization induces the quasi-one dimensional orientations of the spin The atomic relaxation drastically textures. changes surface states. The atomic relaxation also changes the electric field at the surface. Therefore the spin textures and spin-orbit coupling constant of the surface states is strongly affected by the atomic relaxations. We find that the values of the spin-orbit strength and the wavelength of the spin-helix are comparable with those observed for various zinc-blende quantum well structures.

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First-Principles Calculation of Oxide Topological Insulators

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Pyrochlore iridates A_2 Ir₂O₇, (A=Pr, Nd, Sm, Eu, ..., and Y) have attracted great interest for experimental observations of a chiral spin liquid state below 1.4 K and of possible underscreened Kondo effects around 20 K for A=Pr and insulator-semimetal transitions for A=Nd, Sm, Eu, ..., and Y. They are candidate materials for hosting nontrivial topological electronic structures with and without the electron correlation, because of the strong spin-orbit interaction of Ir 5d electrons compared to the bandwidth and the Coulomb interaction. Ad hoc tight-binding and Hubbard model calculations for these materials have suggested a possibility of realizing novel states of matter; (i) a non-Fermi-liquid semimetal with the Fermi surface shrinking into the Gamma point at which two Kramers degenerate quadratic bands meet from below and above, (ii) Z_2 topological insulators with and without a broken cubic symmetry, (iii) a Weyl semimetal and an axion insulator in the presence of the all-in, all-out antiferromagnetic (AF) order. There is a report of the first-principles calculations, based on the linear muffin-tin orbital method, on the pyrochlore iridates. However, it yields an antiferromagnetic order even for Pr2Ir2O7, in sharp contrast to experiments. Therefore, more careful calculations from the first principles are called for to achieve a coherent understanding.

We revisit this issue through extensive fully relativistic LSDA and LSDA+U electronic structure calculations on Y₂Ir₂O₇ and Pr₂Ir₂O₇ (with Pr being replaced with La) by using OpenMX code[1]. With increasing U, a transition from a paramagnetic semimetal to an all-in, all-out topologically non-trivial AF semimetal, and to all-in, all-out topologically trivial Mott insulator occurs. A choice of U=1.3eV explains experiments on a narrowgap AF insulator for Y₂Ir₂O₇ and a paramagnetic semimetal close to an onset of the AF order for Pr₂Ir₂O₇. In the case of U =0 for Pr₂Ir₂O₇, we demonstrate that decreasing the trigonal compression of IrO₆ octahedra, as basically achieved by changing A-site elements, drives successive transitions to the Fermi-point semimetal of an electron and a hole quadratic bands, and then to a cubic Z₂ topological band insulator which we confirmed by Z₂ indexes derived from parity eigenvalues.

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Interface magnetic anisotropy of Nd-Fe-B magnets

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As the most powerful class of permanent magnets, Nd-Fe-B sintered magnets have been used in many applications. However, the origin of their high coercivity is still open for discussion. Since the inside of the crystalline main phase, i.e. $Nd_2Fe_{14}B$, cannot pin the domain-wall motion, microstructural interfaces between the main phase and a subphase will play an important role in exhibiting the coercivity of the magnets. The magnetic anisotropy of a Nd atom is dominated by the anisotropy of the electrostatic potential felt by the 4f electrons of the Nd atom. Thus, it is very important to clarify the electronic structure of interfaces, which determines the electrostatic potential. Since the triple-point phase, one of the sub-phses, is the source of the stray field, i.e. the origin of demagnetization field, we focused the triple-point phase, in particular Nd oxides. We aimed to determine a stable atomic structure and electronic states of interfaces.

In our calculations, the interface consists of $Nd_2Fe_{14}B$ - $(\sqrt{5} \times \sqrt{5})$ and $Nd_4O(001)$ - $(\sqrt{2} \times$ $\sqrt{2}$, where oxygen atoms are located at tetrahedral sites of Nd atoms as showin in Fig. 1 (a). From our results, we find that a disturbance from the bulk structure of Nd_4O near the interface is relaxed, as the distance from the interface becomes longer. This choice is motivated by experiments, where the triple-point phase directly in touch with the main phase is identified as Nd oxides with the fcc Nd sublattice (NdO_x) [1, 2]. We identified that O atoms at the interface prefer to present with Nd compared with Fe. We have also found that the electronic structure inside the main phase is hardly perturbed by the presence of the interface as shown in Fig. 1 (b). Examining the anisotropy constants of Nd at the

interface and inside the main phase, we derived an effective spin Hamiltonian, with which we performed atomistic micromagnetics simulations. The single-ion anisotropy constants due to localized 4f electrons in Nd were calculated by the crystal-field analysis. As for the site-decomposed anisotropy induced by itinerant 3d electrons of Fe, we employed our computationally efficient method [3], where the sum rule is satisfied by including indirect offsite contributions in the second-order perturbation. Considering the anisotropy of Fe sublattice [3], approximately 10% of estimated coercivity is attributed to the effect of Fe sublattice.



Figure 1: (a) The atomic structure of a $Nd_2Fe_{14}B-NdO_x$ interface and (b) depth profile of the magnetic moment within the main phase.

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Large scale ab initio calculations on the fundamental processes of energy convergence devices and on their optimization for high conversion efficiency

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1. Structural, Electronic, and Optical Properties of mixed organic-inorganic halide perovskites. Chemical solutions for working and environmental issues.

We have investigated during the last year several properties of mixed organic-inorganic halide perovskites. In particular we have focused in the possibility of reducing the reported hysteresis in the J-V curve measurements of the perovskite solar cells. We have thus focused on the calculation of systems where the most common organic cation present in these mixed perovskites is replaced by other with a reduced dipole moment. We similarly have investigated the possibility of replacing lead atom in such perovskites with other less environmentally risky metals, according to the aliovalent replacement:

$$2 \operatorname{Pb}(\mathrm{II}) \rightarrow 1 \operatorname{X}(\mathrm{I}) + 1 \operatorname{Y}(\mathrm{III})$$
(1)

We have performed quantomechanic calculations by means of the DFT as implemented in several computational packages. Optimizations and electronic structure calculations have been performed mainly using the Atomic Orbital based Siesta code and the Plane wave based PWscf one.

Our calculations predict the thermodynamic stability of intermediate alloys using molecular organic cations different from methylammonium (mainly guanidinium and formamidinium) that can find applicability in Photovoltaics. Similarly, systems using couples of metallic cations different from Pb(II), that respect the stoichiometry of the initial systems (Eq. 1), are found to have possible applicability Photovoltaics since calculated in the similarities with the parental species MAPbI₃.

2. Atomic scale interface of RuO2/water under electrochemical conditions

Oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) are the key reactions in both the cathode reaction of polymer electrolyte fuel cells (PEFCs) and the photoelectrocatalytic water-splitting reaction. Toward the higher energy efficiency, electrochemical reaction and interface in atomic scale is fundamental and has the possible benefits for designing the materials.

For this purpose, the reaction mechanism of ORR on Ta3N5 (100) surfaces was examined first and then the interfacial structure of RuO2/water under given pH and potential was examined. DFT calculations including the effect of pH and electrode potential are performed using GPAW software. The GGA/RPBE functional and PAW method are used for all calculations. As a result, surface Pourbaix diagram of RuO2/water was obtained with corresponding structure. The results indicate the pH dependent interfacial structure. The reason for such behavior is originated to the stable hydrogen network and electric field effect at the interface. Focusing on the OER potential region, pH condition causes the different Ru formal valence and composition of first water layer because the higher pH condition stabilizes the interfacial structure with lower work function. Such structural difference possibly results in the pH-dependent behavior of OER either through the mechanisms or the probability of starting reactions.

3. Ab-initio investigations on tantalum oxynitrides : novel materials for photocatalysis

Perovskite tantalum oxynitrides ATaO₂N (A = Ba, Sr, Ca) are promising candidates for water-splitting photocatalyst due to their ability to produce hydrogen under visible light irradiation. However, oxygen production has not reported yet, and accordingly further optimization of the band edge positions is mandatory. Previous studies suggest possible modifications of the properties of such materials by changing geometrical structures such as perovskite octahedral-tilting [1] and oxynitride anion ordering [2]. Here, to demonstrate the effects of them in tantalum oxynitride perovskites, we have investigated the structural and electronic properties of CaTaO₂N and MgTaO₂N with various anion ordering, by means of DFT based calculations.

All the calculations were done on VASP with GGA/PBE functional. On-site coulomb interaction U = 5.0 eV was adopted on tantalum d-orbitals.

Among the models with different anion orderings, bandgaps differ up to 1.3 eV in MgTaO₂N and up to 0.6 eV in CaTaO₂N, despite exactly the same chemical compositions, with the former class (MgTaO₂N) characterized by bandgaps larger than the latter (CaTaO₂N). The band structures showed that the octahedraltilting mainly impacts on the conduction band structure and anion ordering impacts on the valence band structure, through the difference in the mixing of tantalum d-orbitals and anion p-orbitals.

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Development and application of first-principles simulator for dynamics in electron transport

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Recently, in the research and development of new electronic devices comprising nanoscale materials, theoretical investigations have attracted much interest. So far, a lot of firstprinciples studies on the electron-transport properties of nanoscale materials were performed and many remarkable results have been reported. However, most of these studies discuss the static characteristics in the steady state, and there remains a lot of uncertainty on the dynamic behavior of electrons flowing across the materials.

In order to examine the dynamic transport properties of the nanoscale materials sandwiched between semi-infinite crystalline electrodes, we improved the impulse response (IR) method [1] which is the dynamic electrontransport calculation method based on the real-space finite-difference approach [2] within the framework of the time-dependent density In the conventional IR functional theory. method, a system connected to semi-infinite jellium electrodes is considered and an impulse wave localized with respect to the transporting direction is prepared as an incident wave. Here, the impulse wave is treated as the linear combination of plane waves with various incident energies, which are the generalized Bloch states in the jellium electrode. After several time steps, the scattering wave function for the incident electron with certain incident energy can be obtained by means of the Fourier analysis of time-evolved wave functions. In this subject, we developed a new algorithm to deal with the initial impulse wave consisting of superposition of the generalized Bloch states in the crystalline electrode. Moreover, we adopted the improved IR method to demonstrate the electron transport in the BNdimer embedded graphene connected to semiinfinite graphene electrodes, where the calculations were performed with a few hundred cores on FUJITSU PREMEHPC FX10 (System C).

As the results, we observed the electrons incident from one crystalline electrode were propagating toward another one and being scattered by the impurity potential of BN dimer. However, it is found that there are some logical errors in the algorithm of calculating the conductance spectrum and the efficiency of the parallel computing is terribly low. Challenges to resolve these problems are in progress.

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First principles calculation of van der Waals interaction in Pt clusters on graphene

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Since the discovery of graphene, a twodimensinal material composed of a hexagonal lattice of carbon atoms, a great deal of effort has been made to apply its peculiar electronic properties to industries. One of the most important examples is application to automotive catalysts, where graphene is expected to influence the catalytic activity of metallic nanoclusters deposited on it. Indeed, it has experimentally demonstrated that Pt nanoclusters supported on graphene shows higher catalytic activity than on other carbon allotropes such as HOPG surfaces and carbon nanotubes [1]. Towards the development of further efficient catalyst materials, there is a compelling need for the microscopic elucidation of the characteristic support effect of graphene on metallic nanoclusters.

The first step to the theoretically understanding of such systems is determination of the structure of metallic nanoclusters, since the catalytic activity is highly dependent on the surface structure. So far the structure of Pt nanoclusters has been extensively investigated with first principles calculation based on the generalized gradient approximation (GGA) [3, 4, 5]. As the size of Pt nanoclusters is increased, however, it becomes more important to consider the influence of non-local van der



 \boxtimes 1: Flat (left) and 3D (right) Pt₇ nanocluster supported on graphene

Waals (vdW) interaction, which is not taken account of in GGA.

Here we report an investigation of the influence of vdW interaction on the stability of Pt₇ nanolclusters supported on pristine graphene, among which two characteristic relaxed structures are shown in Fig. 1. The first principles calculation was performed using STATE codes and vdW correction was included semiempirically via the DFT-D2 method [2]. We adopted a rhombic 4×4 unit cell for a graphene sheet, and $3 \times 3 \times 1$ k points are sampled uniformly. We first confirmed that vertical adsorption of the flat Pt₇ nanocluster shown in Fig. 1 gives the largest adsorption energy, defined by $E_{\text{int}} \equiv E_{\text{Pt}_7/\text{gra}} - E_{\text{Pt}_7} - E_{\text{gra}}$, in good agreement with Ref. [4]. When the vdW correction is taken into account, on the other hand, we found that the three-dimensional (3D) Pt₇ nanocluster (see Fig. 1) becomes more stable than the flat one by 0.63 eV. This means that adsorption of the 3D nanocluster is stabilized by vdW interaction between graphene and Pt atoms directly connected to graphene. Although it has been widely believed that vdW interaction plays a dominant role mainly in weak physisorption in sparse materials, our findings suggest that vdW interaction is also important for metallic nanoclusters on graphene. To investigate the influence of vdW interaction more precisely, we need to adopt more sophisticated treatment such as vdW-DF [6].

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First principles calculation of point defects in electrodes of solid oxide fuel cells

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Acceptor-doped BaZrO₃ shows high proton conductivity under a wet condition and is a promising material used for a proton conductive electrolyte. А problem for realization of BaZrO₃ as the electrolyte is a proton-trapping phenomenon. In the acceptordoped BaZrO₃ systems, it has been reported that a part of the protons are captured around the dopants. This is because there are attractive coulomb interactions between protons and acceptors those have opposite charge states. Such trapping results in reduction of number of charge carriers. In this study, our main purpose is to clarify the proton-trapping phenomena in the acceptor-doped BaZrO₃ by calculations based on density functional theory.

Total energy calculations were performed using the VASP code. Electron-ion interactions were represented by the projector augmented wave method, and the generalized gradient approximation was chosen for the exchangecorrelation functional. Plane waves up to an energy cut-off of 400 eV were used as the basis set for wave functions. Supercells of BaZrO₃ containing 625 atoms, $5 \times 5 \times 5$ unit cells, was constructed for the calculations of defective systems. Only the Γ point was adopted in the kpoint sampling for the supercells. All atomic positions in defective systems were fully relaxed until all residual forces were less than 0.02 eV/Å.

Figure 1 is plots of calculated association energies of dopants (Sc and Y) and proton to distances between the point defcts. According to approaching of the proton to the dopant, association of proton-dopant becomes more stable. A proton is the most stable at the nearest neighbor site from Sc. In case of Y-doped system, the second nearest neighbor site energetically prefer to the nearest neighbor one.



Fig. 1. Dependence of association energies of dopant-proton pairs on distances between defects.

First principles calculations of point defects nearby grain boundaries of alpha Al_2O_3

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Growth of alumina scales on aluminumcontaining alloys in thermal barrier coatings (TBCs) is dominated by inward oxygen and outward aluminum diffusion at grain boundaries (GBs) across the scale. Recent oxygen permeation experiments of α -Al₂O₃ wafers at high temperatures of 1750–1950 K, to elucidate the mass transfer behavior in the GBs, have shown that the diffusing species switches between aluminum and oxygen vacancies depending on the applied oxygen partial pressure. In this study, we investigate the influence of dopant segregation nearby grain boundaries on mass transport in α -Al₂O₃.

Total energy calculations were performed using the VASP code. Electron-ion interactions were represented by the projector augmented wave method, and the generalized gradient approximation was chosen for the exchangecorrelation functional. Plane waves up to an energy cut-off of 500 eV were used as the basis set for wave functions. Atomic configurations of the $\Sigma 31$ grain boundary are shown in Fig. 1. In the present study, we focus on Y^{3+} ion as a dopant, which is known to suppress oxide ion transport nearby grain boundaries. We introduce oxide ion vacancies $(V_{0}^{..})$ at a bulklike region and on the grain boundary of the Y-doped Σ 31 grain boundary model. Formation energies of $V_{\rm o}^{\cdot \cdot}$ are evaluated for the each case. Formation energies of $V_{\rm o}^{\cdot \cdot}$ near the grain boundary are about 1.7 eV lower than those in the bulk-like region. $V_{\rm o}^{\cdot \cdot}$ will accumulate near the grain boundary. In addition, $V_{\rm o}^{\cdot \cdot}$ become more stable at neighboring sites to Y^{3+} ions at the $\Sigma 31$ grain boundary. This result indicates that the segregated Y^{3+} ions act as trapping sites to V_o^{\cdots} . Our calculations clarify the mechanism of mass transport suppression by Y doping in α -Al₂O₃.



Figure 1: Atomistic structures of Y-doped $\Sigma 31$ Al₂O₃ grain boundary.

Simulation of Electronic Properties in Materials for Spintronics

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Graphene is considered to be one of the candidates for spintronics materials. For the device application of the graphene, we need to consider the effect of substrate. In this study, we perform first-principles calculations on graphenes on ferromagnetic Ni substrate.

We first spin polarized density functional calculations on few layer graphenes on Ni and find that the electronic structure of the first layer which touches the Ni (111) substrate is greatly affected by the Ni substrate. On the other hand, the partial density of states of the other layers are close to that of the free standing graphene. By analyzing the partial density of states, we find that the electrons are somewhat transferred to these layers.

Then, we focus on the single layer graphene on the Ni substrate. First, we consider the case that the direction of the magnetization of Ni is perpendicular to the surface ([111]) and find that the spin structure of the graphene is close to the antiferromagnetic structure. This result is consistent with those of our previous study [1].

Next we consider the case that the direction of the magnetization is parallel to the surface. We first carry out calculations without including the spin-orbit interaction (SOI) and next do calculation with the SOI. By analyzing the results of the two calculations, we estimate the Rashba effect. The split due to the Rashba effect is estimated to be 10 meV. There are two experimental results which support large split due to the Rashba effect (225 meV)[2] and small split (less than 45 meV.) Our result supports the latter result [3]. In any case, we find that the Ni substrate has a substantial SOI effect on the mono-layer graphene.

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First principles study on lattice thermal conductivity reduction in multinary zinc-blende-type semiconductors

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By introducing different cation species to Zn sites, a zinc-blende-type semiconductor can be converted from a binary to multinary compound. This system has been drawing much attention since one can create various semiconductors having different properties through this modulation. In this respect, recently Cu_2ZnSnS_4 is considered as a candidate for a thermoelectric material.[1] While its good performance is characterized by the low thermal conductivity which is an order of magnitude lower than ZnS, the lowering mechanism is still an open question. In this study, we dealt with this problem by calculating and comparing the lattice thermal conductivity of three zincblende-type materials, namely, ZnS, CuGaS₂ and Cu_2ZnGeS_4 as presented in Figure 1. To simplify the problem, we kept the averaged mass of the cations. The detailed results will be reported elsewhere. To obtain thermal conductivity, we evaluated the cubic interatomic force constants by finite-displacement methods. It amounts to more than 5000 density functional theory (DFT) calculations of a 64atom supercell with atoms displaced in different directions. This large-scale calculation was carried out on F16 and L16 queue in System B. The DFT calculations were done using the

VASP code[2] with a 450 eV plane-wave cutoff and a Γ -centred $2 \times 2 \times 2$ k-point mesh for ternary and quaternary cases. The Phonopy package was used for structure generation and post-processing.[3]



Figure 1: Schematic view of our approach.

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Study on the capacitance of bilayer grapehene by density functional simulation under electric fields

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Atomic-layer materials such as graphene, MoS₂, and h-BN have attracted great attention because of their potential as electronic devices. Especially, bilayer graphene (BLG) is a promising candidate for a channel material in field-effect transistors because of its high mobility and capability of band gap control by electric fields. In order to develop highperformance devices with the atomic-layer materials, it is necessary to understand the behavior of capacitance at nanoscale in the atomic-layer devices, which is crucial for the circuit operation but have not been understood enough difficult to yet and estimate theoretically.

It has been studied how to improve the on/off ratio of field-effect transistors made of BLG in experiments. They thought that the information of interface states seen in the density of states (DOS) must give them a clue for this, and observed the quantum capacitance of BLG, which is closely related to its DOS, under electric fields. However, their results are difficult to understand: nanoscale information of electronic states, which is difficult to obtain from experiments, seems crucial to understand this. Our objective of this research is to facilitate the interpretation of their experiments using theoretical simulation in nanoscale.

We carried out the simulation of the electronic states under external electric fields on the basis of the density functional theory. An isolated BLG in vacuum is considered.

From the response of electrostatic potential to the electric field, the relative permittivity of the BLG is determined for several field strengths. Interestingly, the relative permittivity is not diverged on graphene sheets, which indicates that the graphene sheets are no longer metallic. As a result of incomplete screening of the graphene sheets, even between the sheets, the relative permittivity is larger than one. Therefore, we conclude that the BLG should be regarded as not a pair of the metallic sheets but a single dielectric material. The modeling from this perspective is necessary when analyzing the BLG system.

Atomic and Electronic Structure of Diamond/Cubic Boron Nitride Interface

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Diamond and cubic boron nitride (c-BN) are two materials having the highest hardness on this planet due to their extremely strong covalent bonding between atoms with a sp³ configuration. For this reason, fabricating diamond and c-BN of a high quality and discovering their novel properties and applications have attracted extensive interest. However, the issues, how diamond and c-BN can actually join at the heterojunction are still unclear. Understanding of these issues will greatly promote the study of combining these two materials for enhanced properties.

Figure shows high-angle 1a а annular-dark-field (HAADF) STEM image of the coherent area viewed from [110] direction. One can note that the interface is epitaxial and atomically abrupt. Since the intensity of an atomic column in the HAADF imaging mode is directly proportional to $Z^{1.7}$ (Z: atomic number), the image contrast is brighter for heavier atoms. By interpreting the image contrast, we find that C is bonded directly to B at the interface. Figure 1b shows a HAADF STEM image of a stacking fault area, from which the atomically abrupt junction (indicated by red arrows) and the direct B-C bonding can be confirmed. The stacking fault is found to locate on the c-BN side, which is attributed to the fact that the c-BN has a lower hardness and stacking fault energy than the diamond.



Fig. 1: HAADF STEM images taken along [11 0] zone axis in (a) the directly bonded coherent area and (b) the stacking fault area.

To gain insights into electronic structure of the interface and offer a deeper understanding of the images, we performed density functional theory (DFT) calculations, taking into account both the B and N terminations for the BN. Adhesion energy calculations reveal that the B-terminated interface (Fig. 2a) has a much stronger adhesion than the N-terminated one $(5.577 \text{ Jm}^{-2} \text{ for the B termination and } 2.906 \text{ Jm}^{-2}$ for the N termination), consistent with the HAADF observations (Fig. 1a).



Fig. 2: (a) Relaxed atomic model for the interface between B-terminated BN and diamond. (b) Total DOS and PDOS of the C, B, and N atom contributions for the relaxed interface.

Calculations of electronic structure predict that there emerge electronic states at Fermi level $(E_{\rm F})$ for both spins, indicating that the interface shows a full metallic character (Fig. 2b). Unexpectedly, the $E_{\rm F}$ lies precisely at a peak position of a band of electronic states, that the interface implying may he superconducting. The electronic states at $E_{\rm F}$ come mainly from the interfacial C sp orbitals and are confined to the interface, forming two-dimensional (2D) electron gas (2DEG) [1]. The 2DEG may be ascribed to the polar discontinuity across interface and may be formed on other orientations. Figure 3a,b shows spatial distribution in electronic wavefunction along [110] and $[11\overline{2}]$ projection [2]. One can note that electrons are spatially separated along [110] direction, yet connected along $[11\overline{2}]$ direction via the hybridization of C sp orbitals, implying that this interface shows a quasi-1D nature in electrical conductivity [3]. Further analysis of the charge density and density difference along $(1\bar{1}0)$ plane reveals that most of charges are localized on C and N atoms, and the charge distribution on each atom is severely distorted toward their neighbors, indicating that the interfacial bonds have a strong covalent character. Moreover, a large number of charges are accumulated along the interfacial B-C bonds and these charges are somewhat more than those along the C-C and B-N bonds in the respective bulks, offering an explanation to the strengthening of the interface.



Fig. 3: Electron density at E_F viewed from (a) $[1\overline{1}0]$ and (b) $[11\overline{2}]$ direction. Charges are found to be confined at the interface.

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First Principles Based Analysis of Electronic Structures and Reactions on Surfaces/Interfaces

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We investigated the electronic structures and reactions on surfaces/interfaces, with the aid of the first principles calculation based on the density functional theory (DFT). In addition, we adopted the quantum dynamics calculation code for atomic nuclei to consider the quantum mechanics behaviors of the oxygen molecules. [1]

At first, we investigated the electronic structures of Pd/ZnO interfaces, which is formed with internal oxidation process. [2] The full-potential linearized augmented plane wave (FLAPW) calculation based on DFT was carried out through WIEN 2k [3] on F16 queue in system B. We installed parallelized WIEN 2K with Intel® MPI Library and Intel® Math Kernel Library. We calculated the O-K edge electron energy-loss spectra at Pd/ZnO interfaces with the corresponding supercell, using TELNES3 program which is implemented in WIEN 2k. We found that the sharp peak appears in the vicinity of 530 eV energy loss. This peak appears in the configuration with O atoms bonding on Pt atoms. This result shows the good agreement with our experimental O-K edge electron

energy-loss spectra.

We also investigated the quantum effects in the O₂ dissociative adsorption on Ag(111) surfaces. [4] We performed the twodimensional quantum dynamics calculations with corresponding potential energy surfaces [5] on P1 queue in system B. We found that there are non-negligible tunneling effects in the dissociative adsorption and significant energy transfer and coupling from vibration to translational motion.

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Oxide electrocatalysts

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In the polymer electrolyte fuel cells (PE-FCs), platinum-alloys are commonly used as the electrocatalyst because of their reasonably high activity and acid-durability. It is considered, however, that development of more active, durable, and cheap catalysts are necessary for the renewable energy society. In this context, the group 4 transition metal oxide, such as zirconia (ZrO_2) , tantalia (Ta_2O_5) , and titania (TiO_2) , has attracted attention. In particular, with the development of introducing oxygen vacancy and nitogen impurity into the sample, the activity for the oxygen reduction reaction (ORR) is improving year by year. However, the structure of the active site and the reaction mechanism are remained unclear yet.

To provide a microscopic explanation, we studied the structure of the crystalline Ta_2O_5 and the oxygen vacancy using the firstprinciples DFT-GGA (hybrid DFT) calculation and found that there are several crystalline structures of comparable total-energy and the vacancy structures, hampering thereby reliable calculation. This year, we have analyzed the structure in more detail and found that the lattice relaxation is exceptionally large and long ranged around the vacant site [1]. This fact, together with the coexisting structures, indicates that larger computational cells are required to perform reliable firstprinciples calculation.

Regarding ZrO_2 , on the other hand, no such difficulty is found. We have performed a first-principles molecular dynamics simulation to investigate the ORR pathway. The result indicates that the oxygen vacancy plays an important role in the ORR mechanism but is concerned with the rate-limiting step such that the vacancy needs to be stabilized more to enhance the ORR activity. We then performed a total-energy calculation on the vacancy-stability, and found that the nitrogen impurity can change the charge state of the vacancy with a effect of stabilizing the vacancy. This result naturally explains the experimental result why the nitrogen can enhance the activity.

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Theoretical material design of transition metal oxides heterostructure based on the orbital distillation effect

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One of the ultimate goals of theoretical physics is designing the materials with novel properties ahead of experimental discoveries. Owing to the extension of computational resources and the development of calculation techniques, it is getting worth tackling this problem. To this end, hetero-structure superlattices are good target because we are able to "tune" their material property artificially.

We have studied the perovskite osmate BaOsO₃ and its (001) super lattice [BaOsO₃]₁/[BaTiO₃]₁ scheming to engineer its physical properties. Here BaTiO₃ works as blocking layer. BaOsO3 has threedimensional cubic symmetry(without rotation or tilting of octahedron) and shows metallic conductivity. By cooling this compound, magnetic susceptibility shows Curie-Weiss behavior without magnetic transition[1]. Previous theoretical study by first-principles calculation suggests the osmate locates in the vicinity of magnetic phase[2]. Theoretically, it can be speculate that the width of the band which intersects the Fermi level decrease by dimensional lowering. This is because that the band structure in the vicinity of the Fermi level is dominated by the $J_{eff}=1/2$ states which is induced by the cooperation between strong spin-orbit coupling effect(SOC) and crystal fields splitting. This $J_{eff}=1/2$ state consists three types of t_{2g} orbitals(d_{xy} , d_{yz} and d_{zx}) and two of them spread along z direction, therefore the prevention of perpendicular

hopping path degrades total band widths of $J_{\rm eff}=1/2$ states. To confirm this speculation, we have performed first-principles calculation for the both of BaOsO3 and [BaOsO₃]₁/[BaTiO₃]₁ using WIEN2k package[3]. Fig.1 shows the band structure and the thick line shows the weight of $J_{\rm eff}=1/2$ states. From these results, the electron correlation effect should strengthen in the super lattice, and it is expected that the possibility of magnetic transition will go up.



Fig.1 Band structure of BaOsO₃(left) and [BaOsO₃]₁/[BaTiO₃]₁(right)

To investigate what types order might be favorable, we have constructed the maximally localized Wannier function[4] to obtain tight-binding t_{2g} orbital model for the super lattice. Fig.2 depicts the band structure around the Fermi level compering the result of first-principles and present model. In this

model, the spin-orbit coupling is taken into account in local hopping term among each Wannier orbitals. Based on this accurate model, we have constructed multi-orbital Hubbard model considering local interaction. Here we consider onsite intra-(inter-)orbital Coulomb repulsion U(U') and Hunds' coupling J and pair-hopping J'. By applying Hartree-Fock approximation to this model assuming $U \sim 1.4 \text{eV}$, $J \sim 0.1 U$, U' = U - 2J and J'=J, we have obtained antiferromagnetic insulating ground state. From this result, we prospect that the property of superlattice $[BaOsO_3]_m/[BaTiO_3]_1$ (m=1,2,...)might change depending on thickness m of the conducting layer.

This work was done in collaboration with Dr. T. Shirakawa and Dr. S. Yunoki.



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Fig.2 Band structure of tight binding model(solid line) derived from maximally localized Wannier orbital in BaOsO₃/BaTiO₃. Dots show the original band structure obtained from LDA calculation.
Numerical simulation of metal oxides redox reaction on various supports

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Redox reaction of metal oxides (MO) such as nickel oxide and iron oxide is one of candidates for energy conversion and storage systems [1,2]. Fuels such as hydrogen and methane reduce MO to metal (M), while oxygen and water oxidize M to MO. During the reduction process energy is stored as chemical energy in metal. On the other hand, thermal energy and chemical energy such as hydrogen are produced in oxidation process. The metal oxides have higher energy densities in comparison with the present lithium ion battery. Therefore, the systems using redox of the metal oxides have attracted much interest. Recently, we reported acceleration of redox reaction of metal oxides with oxide ion conducting supports. For further improvement of redox reaction rate, reaction mechanism of the redox reaction should be clarified. In this study, we focus on oxidation process of metal iron by water vapor. Dissociation of water molecule on Fe(100) surface, i.e., adsorption energies and dissociation barriers, was investigated using the density functional theory (DFT) and the nudged elastic band method (NEB). SIESTA code [3] was used for the DFT calculations. The

generalized gradient approximation (GGA) using the RPBE functional [4] was used as the exchange correlation function. $p(2 \times 2)$ unit cell and vacuum layers of 10 Å was sampled with 2 $\times 2 \times 1$ k-point grid automatically generated using the Monkhorst-Pack method [5]. During relaxation, positions of atoms in bottom two layers were fixed. Climbing image nudged elastic band method (CI-NEB) was used for the calculation of transition state [6]. Crystal structures were visualized using VESTA software [7].





Fig. 1 shows the calculated energy profile of water dissociation on Fe(100) surface. H_2O adsorbed at the top of Fe atom, followed by the dissociation to adsorbed OH and H. Then, OH dissociated to O and H. Dissociation barrier of

OH and recombination of H to produce H_2 were almost the same and highest among the reaction barriers. It was found that acceleration of these reactions might lead to the improvement of oxidation reaction of iron in water vapor atmosphere. The present result can contribute to clarify the mechanism of hydrogen production process using oxidation of iron by water vapor. [2] N. Xu et al., Energy Env. Sci., 4 (2011)4942.

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Synthesis of proton conducting electrolyte and evaluation of ion conductivity of interfaces

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Proton conducting intermediate temperature fuel cells with proton-conducting solid electrolyte (p-ITFC) have been proposed, which is expected to have high material durability and power generation efficiency. In order to utilize it, it is needed to improve its efficiency. For this mission one of the bottleneck is proton conductivity of electrolyte. To improve proton conductivity, I focused on hetero interface between other kinds of electrolytes. There are some reports that oxide ion conductivity was promoted in hetero interface, so in this study I try to check if promotion of proton conductivity in hetero interface occur or not.

As electrolyte SrTiO3(STO) was chosen. To think what happens in hetero structure, there are some phenomenon that affect to proton conductivity. One is segregation of dopant and one is shrinkage of lattice constant. It was proved by a experiment [1] that dopants segregate in hetero structure and it was said that lattice constant shrinkage has good affect on oxide conductivity.[2] In this study proton diffusion in STO was investigated using density functional theory (DFT) and nudged elastic band (NEB) method. DFT calculations were carried out with the SIESTA code^[3]. The double- ζ split-valence basis set with polarization orbitals (DZP) was used in the calculations. The generalized gradient approximation (GGA) using the RPBE functional^[4] was used as the exchange correlation function, and k-points were sampled with 2×2×2 grids using the Monk horst-Pack method ^[5].

First, proton diffusion barrier was calculated in dopant

segregated and non-segregated system using nudged elastic band method. The picture of the both system and diffusion path of proton were shown in Fig.1. and the proton diffusion barrier is shown in Fig. 2.



Fig.1 diffusion path of proton in (a): dopant segregated system and (b): non-segregated system



Fig.2 proton diffusion barrier in (a): dopant segregated system and (b): non-segregated system

Proton concentrate around most stable area and in both the system diffusion paths are ① and ②. The barriers are almost the same in the both system. Thus from this results it can be indicated that dopant segregation has no effect on proton conductivity.

Second, shrinkage of lattice constant was investigated. The diffusion path in the system with lattice constant shrinkage is the same with non-segregated system. In lattice constant shrinkage system, lattice constant is shorter by 5 % comparing to normal system. The proton diffusion barrier in shrinkage system is shown in Fig.3. Here, diffusive path is also ① and ②. The diffusive barrier in path ② is bigger than normal system. It might be because by shrinkage of lattice constant, the path with

low barrier has been lost. Comparing with normal system, diffusion barrier around ① and ② is high in lattice constant shrike system. Thus from this result, it can be suggested that the lattice constant shrinkage does not have good effect on proton diffusion.



Fig.3 proton diffusion barrier in shrinkage system

In conclusion, lattice shrinkage and dopant segregation might not have positive effect on proton diffusion in $SrTiO_{3.}$ There are not so much previous report on promotion of proton diffusion, thus this phenomenon might be difficult to occur. To confirm this, more experimental and theoretical investigation should be done.

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Ab initio molecular dynamics study of molecular dissociation by irradiation of X-FEL

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Recent developments in x-ray free electron laser (X-FEL) have opened up to access to the femtosecond-scale dynamics of molecules. When a molecule containing a heavy atom is irradiated by X-FEL in hard x-ray region, an inner-shell electron is emitted only in the heavy atom and many electrons are ejected from the molecule through the cascade of Auger decay process. The highly-charged molecule becomes quite unstable due to the large Coulomb repulsive force and dissociates quickly into many fragment ions. The fragment ions may convey information about the molecular structure. This technic is referred to as Coulomb explosion imaging. To improve this technic, it is needed to understand about the explosion process of the highly-charged molecule. Under these circumstance, we have investigated the dissociation mechanism of the highly-charged molecule after X-FEL radiation by using ab initio molecular dynamics simulations. In this study, we used iodouracil (I-C₄H₃O₂N₂) as a target molecule. To take into account Auger cascade in the simulation, we gave charges to the system in sequence (charge build up).



FIG. 1. Time evolution of the charge state of the iodouracil.

Figure 1 shows the time evolution of charge state of iodouracil. We calculated kinetic energies for ejected ions of the sequential charged molecule at the beginning, which is measurable physical quantity from experiments. The kinetic energies obtained from our simulation for hydrogen atoms (H⁺), and oxygen atoms (O^+) and iodine atom $(I2^+)$ are about 28 eV, 14 eV and 5 eV, respectively. These values are consistent with experimental results. From these results, the sequential charge build up is thought to be effective. The clarified dissociation simulation the mechanism of iodouracil from a microscopic point of view.

Ultrahigh-pressure structures of liquid oxygen and nitrogen

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Oxygen and nitrogen are infinitely familiar and famous elements because they are high abundant elements in the solar system and closely related to life on earth. Liquid states of these elements consist of diatomic (O₂, N₂) molecules. Under high pressure, breaking bond of these molecules on compression may lead to formation of extended structures. Recently, ultrahigh-pressure (multiterapascal pressure) research have been intensive studied with the recent progress in the experimental and computational methodologies. For the high pressure studies of liquid oxygen or nitrogen, however, structures of these liquid under multiterapascal pressures have not been investigated.

For these reasons, we have performed molecular dynamics (MD) simulations based on density-functional theory (DFT) to investigate the structural and electronic properties of liquids oxygen and nitrogen under multiterapascal pressure.

Figure 1 shows pair distribution functions g(r) of liquid oxygen at 154.1 GPa and 5017.7 GPa obtained by our simulation. At 154.1 GPa, the fist peak at about 1.22 Å reflects the



FIG. 1: pair distribution functions g(r) of liquid oxygen at 154.1 GPa and 5017.7 GPa.

covelent bond in O_2 molecule. With increasing pressure, the second peak at about 2.3 Å, whose positon shifts to smaller *r*. The first peak becomes incorporated into the second peak and changes to shoulder. On the other hand, for liquid nitrogen, the first peak of g(r), which also reflects the covelent bond in N₂ molecule, disappears completely at less than 100 GPa.

This study clarified multiterapascal -pressure structures of liquid oxygen and nitrogen. It also highlighted the difference between structures of these two liquids under high pressure.

First-principles study on the defects in semiconductors

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As the size of devices on integrated circuits decreases, the behavior of dopant atoms make relatively larger effect on the device performance. Especially, it is very important to understand the unfavorable defects including the dopant atoms. The experimental observations on each defect is extremely difficult. One of the major difficulties for detecting dopant configurations is the very weak signals from the defects of very low concentration comparing to those from the matrix semiconductors. However, recently, as a solution for the above problem, it is suggested to use powerful synchrotron radiation facilities to measure the X-ray photoelectron spectroscopy (XPS) signals of defects. On the other hand, there have been few reliable first-principles core-level XPS calculations for impurity defects in semiconductors, because the local potential boundary condition of defect model systems has not yet been sufficiently evaluated. To obtain reliable shifts in the XPS binding energy, it is necessary to take a sufficiently large supercell for a defect.

To investigate the dependence of the substrate semiconductors on the XPS binding energies, we carried out a comprehensive study on the dopant core-level XPS binding energies for defects including B, Al, P, and As in crystalline 3C-SiC[2], and for defects including B, As, P in crystalline Si, using a first-principles calculation with careful evaluation of the local potential boundary condition for the model system. The code used in this study is xTAPP, which is a hybrid paralleled density functional theory calculation program with plane-wave basis[1].

It is found that the relative range of XPS binding energy in SiC is about 4 eV, which is much larger than that of 1 eV in Si. This is because, while the Si is the elemental semiconductor, the SiC is the compound semiconductor and the deviation of the local potential is much larger than that in Si. On the other hand, the variation size of the relaxation energy, where the surrounding wave functions relax under the effect of the hole after the photoelectron emission, is roughly the same for the Si and SiC substrates.

The SiC has many polymorphs. We calculated some defects in 4H-SiC as well as 3C-SiC, and found that the dependence of the XPS binding energy on the polymorphs is not large.

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Geometric and electronic structures of honeycomb sheet consisting of atoms in 14th group

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The discovery of one-atom thick carbon honeycomb sheet, graphene, has triggered the competition to form exotic honeycomb materials and to uncover their hidden properties. Silicene, a two-dimensional (2D) honeycomb sheet consisting of Si atoms, has attracted lots of attention. It is theoretically predicted that a freestanding silicene hosts Dirac fermions [1] and that silicene is also a 2D topological insulator due to the sizable spin-orbit coupling of Si atom [2]. We carried out two projects: (1) exploring of new substrates to form exotic silicene and (2) determination of geometric structure of multilayer silicene.

(1) We investigated the stability of silicene on Ni(111) covered with a hexagonal boron nitride (h-BN) layer by using density functional theory (DFT) calculations. The DFT calculations were carried out by the plane-wave-based Vienna Ab initio Simulation Package (VASP) [3, 4] with the projected augmented wave method [5]. The silicene on h-BN/Ni(111) was modeled by using a

supercell which consists of a silicene layer lying on a h-BN layer on top of a 5-layer Ni slab with a vacuum of 15 Å thick along the surface normal. The positions of atoms in silicene, h-BN, and top four layers of Cu slab were optimized without any constraint until the forces on individual atoms were less than 0.01 eV/Å. In order to weak interface couplings, van dear Waals correction was included. From the total energy calculations for various configurations of silicene lattice relative to the h-BN lattice, we found that the silicene is stable, and that Dirac fermion feature survives similarly to the freestanding silicene.

(2) The multilayer silicene is also attractive because the recent of photoemission experiment has presented a Dirac fermion feature [6]. Two structure models have been proposed for the multilayer silicene. One is a bilayer honeycomb structure in which two buckled honeycomb layers are stacked [7]. The other is very similar to the reconstructed structure formed by the adsorption of Ag atoms on Si(111) [8]. There is a hot debate about the geometric structure. We calculated electronic structures of both models and tried to compare the energy spectrum of multilayer silicene measured by using metastable atom electron spectroscopy (MAES).

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Geometric structure and magnetism of molecules connecting with metal electrode

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Molecule under scanning tunneling microscope (STM) junction provides a model of a single molecule quantum dot. The metal substrate and the tip of STM work as electrodes. This molecular dot can be used as a simulator to manipulate the quantum state of the dot by changing the tip-molecule distance to tune the coupling strengths of the molecule with the electrodes.

We tried to manipulate the Kondo resonance states of iron(II) phthalocyanine (denoted as FePc) on Au(111) [1,2] experimentally. When the tip was far away from the FePc molecule Au(111), a Fano-Kondo (F-K) on antiresonance was observed together with a broad FK resonance. As the tip approached to the central Fe ion of the the F-K antiresonance molecule. gradually became symmetric and a pair of conductance steps appeared in the dI/dV spectrum. The broad FK resonance also disappeared finally when the tip

touched with the molecule. The conductance step was split by applying an external magnetic field vertically to the molecular plane. This indicates that the origin of the step is spin excitation relevance of fine energy structure caused by the spin-orbit interaction (SOI). This evolution reversibly spectral was observed when the tip moved away from the molecule. These results indicate the of Hamiltonian of crossover the molecular quantum dot between the Kondo regime and the regime governed by SOI.

In order to understand the experimental results, we calculated in detail the geometric structure, electronic structure and spin state of FePc in the STM junction by the plane-wave-based Vienna Ab initio Simulation Package (VASP) [3, 4] with the projected augmented wave method [5]. The STM junction was modeled by using a supercell. The STM tip was modeled by a trigonal pyramid consisting of Au atoms. The FePc molecule is located on a four-layer Au slab. To describe the Coulomb interaction at the Fe ion, we used local density approximation +U method. We calculated the geometric structure, density of states and spin state as a function of the position of the STM tip. Approaching the tip to the Fe^{2+} ion, the spin state and the electronic configuration were not drastically changed. In contrast, the position of the Fe²⁺ ion was significantly changed. When the tip was far away from the molecule, the ion was slightly shifted to the Au substrate because of the chemical interaction between them. When the tip was close to the ion, the ion was moved to the tip. We found the switching of the ion position takes place. Looking at the charge density distribution, the electron charges are accumulated at the interface between the ion and the substrate. When the tip was set close to the ion, the accumulation is reduced and instead the charges are accumulated in the region of tip-ion interface. The spectral evolution and the crossover is explained by changing the coupling of molecule and substrate.

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First-principles study on magnetism and atomic structures of transition-metal oxides

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The magnetic spin structures of the Asite-ordered perovskite oxides $YMn_3Al_4O_{12}$ and $LaMn_3V_4O_{12}$, and the isostructural phase transition in $LaCu_3Fe_4O_{12}$ have been investigated by using first-principles calculations.

YMn₃Al₄O₁₂ and LaMn₃V₄O₁₂ both crystallize in cubic Im-3 structure and exhibit antiferromagnetic (AFM) spin ordering at low temperatures. However, the ground-state spin structure is collinear G-type AFM (G-AFM) in YMn₃Al₄O₁₂ whereas non-collinear AFM with rhombohedral R-3 symmetry in LaMn₃V₄O₁₂. In order to clarify the microscopic origin of those spin structures, the electronic structures were calculated based on the densityfunctional theory and the generalized gradient approximation. The calculations were performed on FUJITSU PRIMEHPC FX10 (System C) in the super-computer center of ISSP. The calculations revealed that the magnetic spin structures are determined by Mn-O-Mn super-exchange interaction, which changes the amplitude and sign depending on the Mn valence. In $YMn_3Al_4O_{12}$, the nearest neighbor (NN) Mn³⁺ ions are coupled antiferromagnetically to stabilize the G-AFM structure. In $LaMn_3V_4O_{12}$, on the other hand, 2nd NN pairs of Mn^{2+} ions are coupled antiferromagnetically, which stabilizes the noncollinear AFM spin structure [1].

The isostructural phase transition in $LaCu_3Fe_4O_{12}$ occurs at $T_c = 393$ K, accompanied by decrease in the crystal volume, magnetic transition from AFM to paramagnetism

(PM), and insulator-to-metal phase transition. Furthermore, a similar phase transition also occurs when pressure is applied. Our calculations revealed that the Cu valence is Cu^{3+} in the low-temperature (or larger-volume) insulating AFM phase but Cu^{2+} in the high-temperature (or smaller-volume) metallic PM phase. The change of Cu valence from Cu^{3+} to Cu^{2+} and corresponding charge transfer between Cu and Fe ions play a crucial role both in the temperature- and pressure-induced phase transitions.

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Theoretical elucidation on the full reaction mechanism of threonine synthase

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Molecular mechanisms of the efficient chemical reactions and energy transformations in biological systems are crucially important to be solved not only for biology but also for various application fields including medicine, pharmacy, chemical industry, and material developments, and rapid returns to the society can be expected by the developments of researches. Especially, chemical reactions in enzymes are extremely efficient and highly selective, the detailed understandings for why such abilities are possessed are very important. For example, the reactions in photosynthesis are helpful for the developments of efficient artificial solar systems, and these research areas have attracted a lot of attentions in recent years. X-ray diffraction (XRD) analysis at the Spring-8, x-ray freeelectron leaser (XFEL) at SACLA, high-sensitive EPR and time resolved spectroscopies are the typical cases. However, by these drastic experimental developments, the chemical reaction mechanisms and detections of the proton atoms not easily performed experimentally. are Therefore, whole reaction mechanisms at the atomic level are still unclear for many important biological systems.

On the other hand for theoretical approaches, fine analyses on the stability, dynamics and geometrical structures can be performed in most all cases, and by using modern theoretical methodologies, physical properties which can directly compare to the experimental results can be calculated. For such computational simulations, huge amounts of computational resources are required, however, by utilizing supercomputers (SCs). it becomes easier to perform such heavy theoretical calculations.

We have been performed classical molecular dynamics (MD) and mixed quantum mechanics/ molecular mechanics (QM/MM) calculations using large-scale theoretical models. We have investigated for the (1) oxygen evolving complex in photosystem II, light absorption in photosystem, circular dichroism of heme in myoglobin, reaction mechanism of nitrile hydratase. Their molecular details were successfully elucidated in good agreements with experimental results [1-8]. In this report, the results obtained for the threonine synthase is mainly described in the following sections [1].

Threonine synthase (ThrS) is a pyridoxal-5'phosphate (PLP)-dependent enzyme which catalyzes the last step of the L-threonine biosynthesis. The reaction involves а stereospecific and regiospecific steps and is most complicated among the PLP enzymes. ThrS is characterized as a "product-assisted catalysis", which means that the product phosphate ion enhances the latter catalytic steps, and this mechanism is one of the critically important functions of native enzymes. Exhaustive theoretical search on the intermediate states and the reaction pathways were performed by using the QM/MM (quantum mechanics/molecular mechanics) method for the latter half reactions from PLP- α -aminocrotonate aldimine to the main product of L-threonine and to the side product of vinylglycine (Figure 1). A complete reaction mechanism has been revealed, and we found that (1) PLP-pyridine N1is unprotonated, (2)phosphate ion is monoprotonated, and (3) the protonated amino group of Lys 61 functions as a general acid in the regiospecific protonation at $C\alpha$ of the PLP Schiff base. Phosphate ion maintains a hydrogen bond to the hydroxyl group of the substrate and that contributes to stabilize the main reaction pathway. We found that the hydrogen bond interaction is critically important for the product-assisted catalysis. These findings are very important not only for the understanding of the catalytic reactions of PLP enzymes, but also for all the chemical reactions to improve the reaction



Fig 1. Active site of the threonine synthase. QM atoms are shown in the tube model.

efficiencies and selectivities.

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Defect formation energies due to hydrogen and helium-dopants on interstitial sites in a pyrochlore-type $Y_2Ti_2O_7$ oxide

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Nano-structured ferritic alloys (NFAs) containing a very high density of nanometersized pyrochlore-type Y-Ti-O oxide nanofeatures (NFs) are ones of candidate materials for advanced fission and fusion energy applications [1]. In the present study, in order to assess the relative stability of trapping H and He in Y₂Ti₂O₇, various point defect structures with H and He atoms doped into the tetrahedral and octahedral-interstitial sites and the associated energies, that is indicative of formation energies, defect have been investigated using ab inito density functional theory (DFT) calculations [2] and compared with those of H and He interstitials in iron (Fe) and Fe vacancy (substitutional).

The core-electron interactions are described by the projector augmented wave method (PAW) as implemented in VASP. Convergence tests show that a high energy cutoff of 650 eV and a $5\times5\times5$ Monkhorst-Pack k-mesh for $Y_2Ti_2O_7$ in its conventional cell, and 350 eV and $7\times7\times7$ k-mesh for Fe in its $4\times4\times4$ bcc supercells, are sufficient for both pure bulk and defect calculations.



Fig. 1: Defect formation energies due to H and He doped into $Y_2Ti_2O_7$.

The extrinsic H and He atoms prefer to occupy individual tetrahedral and octahedral interstitial sites, respectively, in Y2Ti2O7, with resulting defect formation energies of 2.87 eV and 1.02 eV, respectively, according to the DFT calculation. In addition, the occupancy of He atom of the octahedral-interstitial in Y₂Ti₂O₇ is more favored than that of tetrahedral, octahedral interstitial or substitutional site (defect formation energies : 4.47, 4.67, and 2.23 eV, respectively) in Fe. On the other hand, the trapping of H at any of the interstitial and substitutional sites in Fe is more favored than those in Y₂Ti₂O₇.

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First-priniples approach to magnetic properties and spin-orbit interaction

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Rare-earth magnet compounds [1]

Large magnetization and high coercivity are required for high-performance permanent magnet. Recently, $NdFe_{12}N$ has been synthesized as a film on top of W underlayer on the MgO substrate [2]. The compound shows better intrinsic magnetic properties than $Nd_2Fe_{14}B$, the champion magnet compound, for wide temperature range between room temperature and the Curie temperature, although thermodynamic stability is a bottleneck for industrial applications.

We have investigated the magnetic properties of $RFe_{12}N$ and $RFe_{11}TiN$ (R=Y, Nd, Sm) by the first-principles method using QMAS code. The calculation is based on the density functional theory with the generalized gradient approximation. The rare-earth 4f electrons are treated as open-core states. The magnetocrystalline anisotropy is evaluated from the crystal field theory. The crystal-electric-field (CEF) parameter A_l^m is computed from the Kohn-Sham potential as

$$\langle r^l \rangle A_l^m = F_l^m \int_0^{R_c} W_l^m(r) \phi^2(r) dr , \quad (1)$$

where F_l^m is a prefactor of the real spherical harmonics, and W_l^m is the radial part of the Kohn-Sham potential at the rare-earth site. The magnetic anisotropy constant is estimated from the lowest CEF parameter A_2^0 as

$$K_1 = -3J(J - \frac{1}{2})\alpha_J \langle r^2 \rangle A_2^0 n_R , \qquad (2)$$

where J is the total angular momentum, n_R is

the concentration of the rare-earth atoms, and $\alpha_J = -7/1089$ (13/315) for Nd (Sm).

We found that the magnetization is enhanced by nitrogenation in all the compounds we have studied. The increment of the magnetic moment depends on R, but does not strongly depend on Ti substitution. The CEF parameter $\langle r^2 \rangle A_2^0$ substantially increases by nitrogenation for R=Nd and Sm. This suggests that uniaxial (in-plane) anisotropy is induced in the Nd (Sm) compound.

Trigonal Tellurium under pressure [3]

Trigonal tellurium has characteristic structure. Helical chains are arranged in a hexagonal array. The unit cell contains three atoms. The space group is $P3_121$ or $P3_221$, and there is no inversion symmetry.

We have studied the electronic states of tellurium using first-principles calculation. The calculation is based on the fully relativistic density functional theory in the local density approximation, and the GW self-energy correction is added on top of it. The Hamiltonian is represented in the maximally localized Wannier basis, and interpolated for studying energy levels at arbitrary k point.

When the spin-orbit interaction is neglected, the material undergoes insulator-semimetalmetal transition under pressure. As the pressure is increased further, a Dirac cone is formed at certain pressure in the metallic phase. When the spin-orbit interaction is included, the transition pressure decreases, and a Weyl semi-metallic phase appears between the insulating phase and metallic phase.



Figure 1: Phase diagram of trigonal tellurium under pressure. The vertical axis is the scale factor of the spin-orbit interaction.

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Pt adsorption sites in rutile-TiO₂ (110) surface

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The (110) surface of rutile TiO_2 is often used as a model system for fundamental research in the fields of surface science and catalysis [1-3]. Therefore, adsorption of metal atoms and clusters on the surface and their catalytic functions have been well investigated by means of both experimental and theoretical approaches. In the present study, Pt adsorption on the surface was theoretically investigated from first principles.

All the calculations were performed on the basis of the first-principles projector augmented wave (PAW) method implemented in the VASP code [4]. The plane wave cutoff energy was set to be 500 eV. The 3*d*4*s* orbitals for Ti; 2*s*2*p* for O; and 5*d*6*s* for Pt were treated as valence states. The generalized gradient approximation (GGA) parametrized by Perdew, Burke, and Ernzerhof [5] was used for the exchange-correlation term with +*U* correction for Ti3*d* electrons (U = 5.8 eV) [6]. A (2×4) surface slab with 7 cation layers and a 14 Å vacuum layer was used with a 2×2×1 grid for k-point sampling in the Brillouin zone.

Possible adsorption sites of a single Pt atom on the TiO_2 (110) surface and the calculated adsorption energies at the individual sites were shown in Fig. 1. In the stoichiometric surface without oxygen vacancies (sites 1–6), the hollow1 site has the highest adsorption energy. On the other hand, a Pt atom tends to be adsorbed to oxygen vacancies in the reduced surface, whose adsorption energies are \sim 1 eV higher than those at the hollow1 site. This indicates that the surface off-stoichiometry should greatly influence on the Pt adsorption, possibly leading to change in the catalytic function.



Fig. 1: Possible Pt adsorption sites on the rutile TiO_2 (110) surface. Two kinds of oxygen vacancy sites were considered in addition to the six sites on the stoichiometric surface. Energies in parentheses are the Pt adsorption energies at the individual sites.

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Search for new electronic properties of new nanoscale interfaces

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In 2014 we studied the electronic states of SnTe and PbTe(001) monolayers.

Recently topological crystalline insulators are extensively stuided. Topological crystalline insulator (TCI) is a concept introduced by Fu [1]. Electronic states of insulators are classified according to topological numbers defined by point group symmetries of crystals. The first realistic materials of TCI are SnTe and its alloy with Pb. They were theoretically proposed and have been experimentally verified. They are three-dimensional materials. Recently twodimensional (2D) materials of TCI are theoretically predicted, and their new applications were proposed [2]. However, they have not been materialized experimentally. We theoretically studied electronic states of 2D TCI thin films.

The proposal of 2D TCI is based on electronic-state calculations for free-standing thin films [2]. When we make some experiments or devices using 2D TCI, it would be necessary to place them on substrates or embed in materials. In contrast to the topological insulators whose topological character is protected by the time-reversal symmetry, the topological character of TCI is guaranteed by crystal symmetries of systems which is easily broken by the interaction with substrates and environments. Therefore it is important to study the effect of substrates and environments on electronic structures of 2D TCI. In this study we calculated electronic states of SnTe and PbTe monolayers with supports [3].

We calculate electronic states of isolated monolayers assuming planar structures by a density-functional method. We find that the PbTe monolayer has edge states that are characteristics of TCI. However, geometrical optimization shows that the planar structure is unstable. Buckling occurs and the mirror symmetry is broken. In order to maintain the planar structure we consider structures of monolayers with supports. We choose alkali-halide surfaces as supports. Figure 1 show a band structure of a SnTe monolayer wire sandwiched between two NaBr surfaces. Edge states are present in the band gap between the valence and conduction bands, which suggests that this system is a 2D TCI. Geometrical optimization shows that the planar structure is stable in this system.



Figure 1: Band structure of a SnTe monolayer wire sandwiched between two NaBr surfaces.

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Electronic structure of β -FeSi₂(100) surface

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Recently the authors' group found the formation of β -FeSi₂(100) on Si(001) prepared in ultra-high vacuum, using scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED) [1]. Using Simulation Tool for Atom TEchnology (STATE)-Senri [2] in SCC-ISSP system A, the author calculated total energies and STM images for β -FeSi₂(100)1x1 with adatoms (20 models, 66 atoms/model) and without adatoms (1 model, 64 atoms), in order to survey the surface structure.

The details for the calculations are described in Ref. [1]. The calculated substrate structure consists of 1st-layer Si (8 atoms per $\beta(100)1x1$ unit-cell)/2nd-Fe (2 atoms)/3rd-Fe (2)/4th-Si (8)/5th-Fe (4)/6th-Si (8)/7th-Fe (2)/8th-Fe (2)/9th-Si (8)/10th-Fe (4)/11th-Si (8)/12th-H (8). The atomic positions were relaxed except those in the last three layers.

Two hollow-site models (named as H₃ and H₄, and they were almost degenerated) were found to be stable for both Fe and Si adatom models, having p2 symmetry. However, the experimental LEED results require p2gg symmetry, thus these models can be denied. Only the one candidate, WO model (without adatoms) with p2gg symmetry, was consistent with the STM and LEED results, moreover, indicated almost the same structure obtained by LEED I-V analysis [1]. Therefore, we can state the WO model is the surface structure of β -FeSi₂(100).

The author also calculated the k-resolved atomic orbital based local density-of-states (k-AO-LDOS) [3], to identify surface electronic states. A k-AO-LDOS, $\rho(k, E, i, l)$, is a function of a wave vector k, energy E, atom species i and orbital of the *i*-th atom l. k-AO-LDOS was averaged over the LDOS of atoms (number of which is N) within a layer (or a slab) and summed over the corresponding orbitals of the atoms,

$$\rho(k,E) = \frac{1}{N} \Sigma_i \Sigma_l \ \rho(k,E,i,l).$$
(1)

When *i* runs over all atoms in the slab, Eq. 1 shows $\rho_{tot}(k, E)$ ($N_{tot} = 64$) for the all atoms, while the topmost atoms only, $\rho_{surf}(k, E)$ ($N_{surf} = 8$) for the surface atoms. In order to enhance the k-AO-LDOS weight of the particular layer, *i.e.*, surface state components, the surface k-AO-LDOS was squared and normalized on the total k-AO-LDOS. This partial k-AO-LDOS was defined as,

$$\rho'(k,E) = \frac{N_{surf}}{N_{tot}} \frac{\rho_{surf}}{\rho_{tot}} \ \rho_{surf} = \eta \ \rho_{surf} \quad (2)$$

The partial k-AO-LDOS $\rho'(k, E)$ predicted some surface-states dispersions clearly even in the bulk projection [1]. One of them exists in the band gap crossing the Fermi level, which leads to metallic nature. Indeed, a previous angle-integrated photoemission measurements indicated the metallic behavior [4].

The author thank Prof. Morikawa in Osaka University, Dr. Yanagisawa in Ryukyu University, and Dr. Hamada in NIMS for their great support in STATE-Senri calculations.

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Bonding states of organic molecules adsorbed at defects on metal surface

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Organic molecules are of great interest as new material for semiconductor and functional devices. Aromatic molecules on metal and semiconductor surfaces are typical interfacial systems to be benchmarked. It is useful to elucidate the electronic states and structure of such heterostructure at the nanometer scale.

We take three-dimentional aromatic molecules, carboran and its derivative, on a stable metal surface for future functional applications. In the current project, we estimated the stable structure in adsorption, and bonding energy in terms of the bonding site by means of first principle electronic simulation partly executed on the Facility of Supercomputing Center at the Institute for Solid State Physics (SCC-ISSP).

We used Vienna Ab initio Simulation Package (VASP) code. Molecules of *p*carboran-thiol and decamethyl carboran-thiol are adsorbed on Au(111) slab models (The former is shown in Figure 1.) The size of the slab was larger enough than the inter-molecular size of crystalline, so that this structure represents the isolated adsorption at the dilute coverage. The *p*-carboran-thiol is preferably adsorbed at the three-fold hollow site slightly shifted from the center. The binding energy of this molecule is 1.66 eV (with H-dissociation canceled out). A sharp electronic state of Au-S bond lays at -1.8 eV from Fermi level.

The decamethyl derivative has much weaker adsorption energy. This instable adsorption to the flat terrace is due to steric effect of ten methyl groups on the surface. This suggests that the decamethyl derivative is hard to be adsorbed on the terrace at room temperature. This result is consistent with our observation with a scanning tunneling microscoe (STM).



Figure. 1. Stabilized structure of *p*carboran-thiol adsorbed on Au(111) surface. (a) top and (b) bottom views.

First-Principles Molecular Dynamics Simulations on Water Dissociation in Water-Bi-Layer on Stepped Pt Surface

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Water interaction with Pt surface plays important roles in many catalytic surface reactions. corrosion processes, and electrochemistry. Recently, intact adsorption and dissociation of water on flat Pt have been extensively studied by both experiments and simulations [1, 2]. A recent study on adsorption and dissociation of water at the edge of Pt(211) surface showed that the dissociation energy is 0.2 eV for a dimer and nearly zero in the case of a trimer [3]. Moreover, water adsorption on a stepped Pt(111) surface, which is observed after deposition of Pt by X-ray diffraction [4] and commonly occurring in realistic situations, is not well understood.

In this study, we use first-principles simulation tool for atom technology program package (STATE) to elucidate the adsorption and dissociation of water on a stepped Pt(111) surface and between Pt/SiC interface during the etching of SiC in water before molecular dynamics simulations. The calculations are based on the density functional theory within a generalized gradient approximation of Perdew et al. Barrier height is evaluated by means of climbing image nudged elastic band method [5]. A stepped Pt(111) surface composed of 3-layer slab, in which the two topmost layers are kept fixed to mimic the bulk. A step-and-terrace 3C–SiC (111) surface was used as a model for the simulation as shown in Fig. 1. The model is periodically repeated unit cells of four bi-layers. During the simulation, the two topmost atomic layers with terminated surface atoms were allowed to fully relax, while the remaining atoms were kept fixed to maintain the substrate structure.





In this study, we focus on the reaction pathways and reaction barriers of the interaction between H_2O molecules and OH-terminated step edge Si with the present of platinum (Pt) catalyst in the calculation model. The adsorption of water on a stepped Pt surface is preferentially at the step edge of Pt, stabilized by the effect of chemical bonds with Pt and hydrogen bonds. The results show that the barrier height of water dissociation on Pt affected by the distance of Pt and SiC surfaces. The shorter distance between Pt and SiC surfaces, the smaller the barrier height. The adsorption and dissociation of water at Pt/SiC interface play important roles in etching of SiC in water.

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Electronic Structure of Rare Earth Magnets

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The most important permanent magnet materials up to now is Nd₂Fe₁₄B for its high energy product. It, however, has a problem that Dy, which is a rare element, must be added to keep the good performance at operating temperature of around $200 \sim 300^{\circ}$ C. Decreasing the content of Dy from Nd₂Fe₁₄B magnets is a big issue. Yet another candidate of high efficiency permanent magnet materials is $Sm_2Fe_{17}N_3$. It shows much larger magnetic anisotropy and higher Curie temperature than $Nd_2Fe_{14}B$, although its saturation magnetization is slightly smaller than that of $Nd_2Fe_{14}B$'s. Unfortunately, $Sm_2Fe_{17}N_3$ is not chemically stable at high temperature, which prevent us to produce permanent magnets by sintering.

In order to design permanent magnet materials that meet the requirement for new generation permanent magnets, the mechanisms that govern the magnetization, Curie temperature, and magnetic anisotropy of existing permanent magnet materials must be revealed. This is not an easy task since those magnetic systems contains rare-earth metals as an ingredient. One of our main efforts concern with how to deal with f-states of rare-earths in the framework of the density functional theory (DFT). We have developed the method of self-interaction correction (SIC) and the optimised effective potential (OEP) method within exact-exchange (EXX) and static RPA (sRPA) schemes[1].

Figure 1 shows the structure of $Nd_2Fe_{14}B$ and some of exchange coupling parameters calculated in the framework of SIC. The couplings between Nd and Fe are one order of magnitude smaller that those between Fe's. Although



Figure 1: Some of calculated exchange coupling parameters of Nd₂Fe₁₄B.

these values are calculated in the framework of SIC-DFT, it is possible to map the degrees of freedom of local magnetic moments to the Heisenberg model. From this mapping the finite temperature behaviour of magnetization and magnetic anisotropy can be analysed. Thus, it is speculated that that the exchange coupling between Nd and Fe should play an important role for the high-temperature behaviour of the magnetic anisotropy.

The magnetic anisotropy of $\text{Sm}_2\text{Fe}_{17}\text{N}_3$ is also calculated using SIC-DFT. The role of N for the system to exhibit the uniaxial anisotropy are discussed in detail within the same framework.

The calculations are performed using system B of the ISSP supercomputer systems and KKR-Green's function code (AkaiKKR).

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A First-principles study on exchange stiffness constants in magnetic films

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Recently, fully epitaxial Co₂Fe_xMn_{1-x}Si $(CFMS)/Ag/Co_2Fe_xMn_{1-x}Si$ multilayers for current perpendicular giant magnetoresistance (CPP-GMR) devices were fabricated by systematically changing the Fe/Mn composition ratio x, and the highest intrinsic GMR ratios, 184% at 30 K, were observed in the device with x=0.4 and $t_{CFMS}=3(nm)[1]$. However, a reduction of the GMR ratio of 58% was found at room temperature (RT). One possible reason of the large temperature dependence of the GMR ratio in CFMS/Ag/CFMS multilayer is thermal fluctuation of the interfacial magnetic moment providing the spin-flip scattering and reducing the spin polarization of the CFMS/Ag interfaces. In order to elucidate the mechanism of the spin-flip scattering at the interfaces, we theoretically investigate interfacial spin-flip scattering of magnetic films caused by the noncollinear magnetic structures as a result of thermal fluctuation of the local spin-moment.

To estimate the exchange stiffness of the interfacial spin-moments, we calculated the increase of the band energy $E(\theta)$ relative to the collinear-spin system (θ =0) as a function of the angle of local moments θ for interfacial layers of CMS/Ag(001) and CFS/Ag(001) junctions with Co, MnSi and FeSi terminations

using the quantum code ESPRESSO[2]. We constructed multilayer CMS/Ag and CFS/Ag structures containing seventeen atomic layers of CMS or CFS and nine atomic layers of Ag. Other parameters of the first principles calculations are shown in Ref. [3].



Fig. 1: Increase of band energy as a function of the angle of local spin moment Co₂XSi/Ag(001) (X=Fe,Mn) interface. As can be seen in Fig.1, the Co termination of CMS/Ag interface and FeSi termination of CFS/Ag interface show a weak dependence of band energy with increasing θ , indicating the relatively small exchange stiffness constant of these interfaces. The small exchange stiffness constant at interfaces will provide a thermal fluctuation of interfacial spin moment, leading to the reduction of GMR ratio at RT.

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First-Principles Modeling on Emerging Memory Devices

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Superlattice phase change memory (superlattice PCM) consisting of (GeTe)₂/Sb₂Te₃ stacked structure is one of the most promising candidates for nextgeneration non-volatile memories and it has received considerable attention in recent years [1,2]. The memory operations are attributed to small structural change between two atomic configurations before and after switching. Therefore, the energy required for switching between higher and lower resistive states is much lower than that of conventional PCMs utilizing phase transition between crystal and amorphous phases [3]. However, the reaction pathway on the switching of superlattice PCM has not yet been clarified and the detailed analyses of the structural transition between high-resistive and lowresistive states are prerequisites for fully understanding the switching mechanism.

In this work, we investigated the switching process of superlattice $(GeTe)_2/Sb_2Te_3$ PCM using the first-principles electronic states calculations. The atomic structures and the electronic states were calculated by VASP code [4], which is based on density functional theory with plane-wave basis sets, PBE-type exchange-correlation functional and the projector augmented-wave method. For the calculations, *k* points of 8 x 8 x 4 Monkhorst-Pack grid were used and the cutoff energy was 500eV.

high-resistive and low-resistive states are not stable but metastable [5]. Therefore, the superlattice (GeTe)₂/Sb₂Te₃ PCM can do cyclic operations due to the metastability. In addition, we clarified the structural transition process between high-resistive and lowresistive states. The transition process is shown in Fig. 1. First, the centered Ge and Te atoms in the low-resistive state move vertically, approaching to the transition state which consists of a honeycomb double layer (Fig. 1(a) \rightarrow (b)). Next, the honeycomb layers in the double layer slide in different directions and rotate by 60 degrees (Fig. 1(c) \rightarrow (d)). Finally, the Ge and Te atoms move vertically again, resulting in the highresistive state (Fig. 1(e) \rightarrow (f)). The opposite process is the same. The validity of our proposal was shown from the detailed analyses of the potential energy surface and electron-density distribution.

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We found that atomic configurations of

Figure 1: Structural transition process of superlattice $(GeTe)_2/Sb_2Te_3$ phase change memory between high-resistive and low-resistive states.

Thermo-Chemical Wear Mechanism of Diamond Cutting Tool

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Demand has been increasing for highly durable molds of heat-resistant materials for complex and precise optical components with high aspect ratio. Diamond is the only ideal cutting tool material for high efficient ultraprecision cutting of complex threedimensional metal works. However, it is well known that diamond cutting tool shows severe wear in cutting of heat-resistant materials such as ferrous metals and nickel.

On the other hand, in cutting of electroless nickel deposits (Ni-P), which is used as a material of precision molds, remarkably less tool wear is observed than in case of pure nickel [1,2]. Phosphorous addition should have an important role for tool wear suppression. However, the essential mechanism of wear suppression has not yet been understood well. To understand the wear mechanism of diamond cutting tool in machining of nickel and ferrous metals is very much meaningful to realize useful fabrication technique of the precise and durable molds with high accuracy and low cost.

Single grain cutting tests and erosion tests suggest that the wear occurs not by mechanical process but by thermo-chemical one [3-5]. Therefore, in order to reveal the mechanisms of the initial stages of wear process and wear suppression by phosphorous addition, ab initio molecular dynamics calculations of chemical reaction on diamond surface in contact with Ni and Ni-P surfaces were carried out using double-grid method for real-space electronicstructure calculations proposed by Dr. T. Ono of Osaka University [6].

A C₁₀H₁₄ cluster, shown in Figure1, is used as a model of diamond (100) surface. The atom at the bottom of the model is the radical carbon interacting with metal surface. The dangling bonds of the other carbon atoms of diamond are terminated by hydrogen atoms. White and yellow figures express atomic and bond populations, respectively. The dimensions , $x \times$ $y \times z$, of Ni (100) surface model is $2a \times 2a \times a$, where a is lattice constant of Ni. The model has periodic boundaries in *x* and *y* directions and aperiodic boundary in *z* direction. The atomic populations of all Ni atoms are almost 10.0.

Figure 2 shows the optimized atomic configuration of the diamond cluster interacting with Ni and Ni-12wt%P surfaces. By the



Fig.1 Model of diamond (100) surface



Fig.2. Effect of phosphorous addition to interaction with diamond

interaction with Ni, the atomic population of radical carbon increases to 4.91 from 4.11 and those of Ni decreases to 9.73. The result suggests that the strength of ionic bond between carbon and Ni increases. As the population of back bonds of radical carbon decrease to 0.76 from 0.89, the strength of covalent bond of back bonds decreases and the radical carbon has a chance to dissociate from the diamond surface when it has a large kinetic energy due to cutting temperature. On the other hand, in case of interacting with Ni-P, both of decrease of back bond population and increase of atomic population of radical carbon are remarkably suppressed The result suggest that phosphorous addition reduces the dissociation of carbon atoms on diamond surface.

The dissociation energy of the radical carbon was estimated as shown in Figure 3. Diamond model was lifted up from the stable state interacting with work material leaving the radical carbon on work material surface to a position where the force acting to the radical carbon changes from upward to downward direction. The radical carbon is considered to be dissociated at the position. The dissociation energy can be estimated from the difference between the total energy of the system



Fig.3 Estimation of dissociation energy of radical carbon atom

composed of diamond and work material at the stable state and that at the dissociating state. Although the atomic structure was not optimized pulling in up process, the dissociation energies of radical carbon by different work materials can be relatively compared. The dissociation energies estimated are 5.01 eV for diamond-Ni system and 5.70 eV for diamond-Ni-P system, respectively. The result suggests that the wear of diamond cutting tool in cutting of Ni-P is less than that in cutting pure Ni.

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Ab initio Lattice Anharmonicity in Iron-bearing Bridgmanite at High Pressure Haruhiko DEKURA

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Iron-bearing Bridgmanite (Mg,Fe)SiO₃ is believed to be the most constituent mineral in the earth's lower mantle. Determination of the phonon transport property, i.e., lattice thermal conductivity (κ), of the material should be therefore a key to understanding the dynamics and evolution of the earth's deep interior. Lattice anharmonicity owing to the phononphonon interaction strongly relates the phonon transport. The primary purpose of this project in this period is to determine the anharmonic properties of the iron-bearing system at a deep mantle pressure of about 100 GPa.

We have performed density-functional theoretic calculations combined with the LDA+U method [1] and have extracted the large number of anharmonic force constants (AFC) by higher order derivatives of the adiabatic potential surface [2]. All of the calculations were performed using the QUANTUM-ESPRESSO package [3]. Figure 1 shows The simulation cell of $(Mg_{0.9375}, Fe^{2+}_{0.0625})SiO_3$ that includes 160 atoms was adopted in this study. The ferrous iron was treated in the high spin state (S = 2).

During this period, we have succeeded in the determination of about 40% of the total number of AFC (~220,000) to nearest neighbor shell by the use of supercomputer (system B). Our preliminary results show that the amount of each AFC strongly varies from bond to bond. In addition, we have found that the average value of AFC is about 20% bigger than that of the iron free system, i.e., MgSiO₃ Bridgmanite, indicating a moderate decrease in κ accompanied with the iron incorporation. We will continue to promote this research in the next period.



Fig. 1: Crystal structure of iron-bearing Bridgmanite $(Mg_{0.9375}, Fe^{2+}_{0.0625})SiO_3$ optimized at 100 GPa.

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Theory of magnetic and electronic structure for Mn-based ordered alloys with Cu₃Au-type crystal structure

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The Mn-based ordered alloys Mn₃X (X=Pt, Rh, Ir), which all have Cu₃Au-type crystal structure, are frustrated itinerant magnets with an octahedral configuration of Mn local magnetic moments. Neutron diffraction experiments [1] suggest that below the Néel temperatures T_N , Mn₃Rh and Mn₃Ir exhibit a single ordered phase: triangular magnetic structure with Γ_{4g} symmetry. On the other hand, Mn₃Pt exhibits two ordered phases: triangular magnetic structure for T < 400 K and collinear antiferromagnetic structure for 400 K < T < 475 K, the latter phase accompanying tetragonal distortion with volume expansion.

To clarify the physical origin of the magnetic structures of these alloys from the theoretical point of view, we have investigated the temperature dependence of the magnetic and electronic structures by means of the firstprinciples molecular dynamics (MD) approach for itinerant magnets [2]. The theory is formulated by incorporating the first-principles TB-LMTO Hamiltonian into the MD approach for itinerant magnets on the basis of the functional integral method and the isothermal MD technique. The MD approach allows us to determine automatically the magnetic structure of a large system with several hundred atoms in a unit cell at finite temperatures.

In the present MD analysis, we solved the isothermal MD equations of motion by using site-dependent effective medium in order to treat the magnetic phase transition correctly. We used the recursion method to calculate the local electronic structure in determining the site-dependent effective medium and in calculating magnetic forces at each time step of the MD equations of motion. Because the timeconsuming recursion process consists of parallelizable loop calculations, we utilized the MPI parallel calculation scheme in the recursion calculation. The MPI parallel process is found to be quite effective in saving computing time because more than 90 % of the CPU time concentrates on the recursion calculation.

We have calculated the electronic and magnetic structure for a system with 4 \times 4 \times 4 fcc lattice with fixing the crystal structure and lattice constant to their room-temperature values. At sufficiently low temperatures below T_N , Mn_3X (X = Mn, Rh, Ir) all exhibit the triangular magnetic structure, being consistent with experiment. With increasing temperature from 25 K, Mn₃Pt exhibits a secondorder transition to another noncollinear ordered phase around 350 K, accompanying a development of Mn-Eg DOS at Fermi energy $E_{\rm F}$. This is in contrast with the result of previous calculation using uniform effective medium which shows a first-order transition to a lowmoment ordered phase. Mn₃Rh and Mn₃Ir, on the other hand, show no sign of a magnetic phase transition up to $T_{\rm N}$. Further analysis on the magnetic structure of these alloys are now in progress.

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First-principles calculation of atomic arrangement and electronic structure in ceramic grain boundaries

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Grain boundary (GB) is lattice defect in crystalline solid. Atomic arrangement at GB becomes different from that in crystal bulk, and various properties also become different. Some researchers have proposed that this point can be used for obtaining superior physical properties. An example can be found in Ref. 1. With this viewpoint, in the present study, I tried to modify the atomic arrangement and the electronic structure of a GB in SrTiO₃ (STO), which is the prototypic perovskite material by means of first-principles density-functional theory (DFT) calculations.

We chose the [001]/(310) symmetric tilt GB of STO for this study. First, stable atomic arrangement and density of state (DOS) for the undoped GB (Fig. 1 (a)) was calculated. Next, ruthenium (Ru) doped GB (Fig. 1 (b)) was studied. DFT calculation was carried out using the VASP code. Here, generalized gradient approximation (GGA) potential was used. The GB supercells contained 100 atoms.

Figures 2 (a) and (b) show DOS for both of the GBs. In the case of undoped GB, there is a band gap of 1.1 eV. This is quite close to the value calculated for STO bulk crystal, and it is therefore considered that the GB electronic state is not significantly altered. Underestimation of the band gap value from the experimental one of ~ 3.3 eV is due to error caused by GGA.

On the other hand, for the Ru-doped case (Fig. 2(b)), due to creation of extra electronic state in the band gap, there is no band gap. It is considered that electronic state of the GB is metallic. It is therefore suggested that if this kind of GB structure can be fabricated, metallic electrical conduction confined within GB plane may be observed.



Fig. 1: Grain boundary supercell of $SrTiO_3 \Sigma 5$ [001]/(310) GBs used in this study. (a) The undoped and (b) the Ru-doped cases. Figure is drawn using VESTA [2].



Fig. 2: Density of state of the GB supercells. (a) The undoped and (b) the Ru-doped cases.

References

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Electronic State and Proximity Effects around Interface in Layered Superlattices

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The purpose of the present research is to elucidate characteristics of electronic state in superlattices with layered structures, in particular, to illustrate proximity effects of each layer on adjacent layers in the superlattices. This research of a first-principles electronic structure calculation is performed by means of the Korringa-Kohn-Rostoker (KKR) Green function method within the framework of the local spin density (LSD) functional formalism.

The calculation by means of the KKR method was so far carried out for superlattices of ferromagnetic layers with nonmagnetic spacer layers such as Fe/Cr, Fe/V, Fe/Cu, ... ones, with magnetizations of two successive Fe layers being aligned parallel or antiparallel. Oscillatory interlayer exchange coupling between ferromagnetic layers with respect to spacer thickness was investigated, and relation between bulk effects inherent in the spacer layer and the proximity effects due to the ferromagnetic layers was analyzed. In the calculation, every atom in a monolayer stacked in the superlattices is assumed to be equivalent, and there is one site in each monolayer. This assumption can be justified for the superlattices with ideal interfaces without structure, but not for those with realistic interfaces with structures like steps, islands, or such, and hence there are two or more sites in each monolayer for the superlattices with realistic interfaces.

A need of the calculation for superlattices with more sites in each monolayer arises also for layered superlattices of ordered alloys or compounds, which now attract broad interests particularly in viewpoint of spintronics. We then start preparation of the calculation for superlattices with more sites in each monolayer, which results in increase of the number of atoms in a unit cell and involves vast increase of computation times. In the preparation of the calculation, installation of parallelization with use of the OpenMP into program codes of the KKR methods is intended, together with parallelization with use of the MPI which was already achieved, that is, installation of hybrid parallelization is intended.

The installation of the OpenMP is in progress and will be achieved in the next term, and then the proximity effects in the superlattices with realistic interfaces will be investigated to elucidate the roles of the interfaces in the superlattices. The calculation will be carried out for Fe superlattices with steps, and magnetic frustration caused by the steps is investigated, in particular reference to possible mechanism of increase of total magnetization of the Fe layers, where fcc(001) or fcc(111) superlattices are considered together with usual bcc(001) ones and difference between those superlattices is to be analyzed. In addition, the calculation will be carried out for layered superlattices of ordered alloys, such as fcc(001)superlattices consisting of Fe and FePt layers, in particular reference to ferromagnetic or antiferromagnetic coupling between layers and within a monolayer.