Internatinal Frontier Center for Advanced Materials

Head : Prof. **Hidetoshi Fukuyama** (2003. 10～)

【Staff Members】

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Prof. Hidetoshi Fukuyama; Prof. Mingwei Chen; Res. Assoc. Kehui Wu (~2005.1.31)

Researcher LUPU Nicoleta; (15)Visiting Profs ; 2 Part-time employees

《Division of Advanced Research》

Prof. Akihisa Inoue; Prof.Toshio Sakurai; Prof. Sadamichi Maekawa

【Research Activities】

The IFCAM members have been actively conducting individual research projects while serving as the IMR think-tank especially to promote the coordinating activities with the IMR. The followings are the main activities in the FY 2004.

1) Research Workshops

"IFCAM International Workshop on Electronic Properties of Cobalt Oxidies," June 3-4, 2004, IFCAM.

"IFCAM Mini Workshop on Nano-science and technology," June 21, 2004, IFCAM (Sakurai Lab, Division of Advanced Research).

IFCAM Mini Workshop on "Quantum Transport," Aug 23-26, Sep 30-Oct 1, Oct 22-24, 2004, IFCAM (Fukuyama Lab, Division of Planning and Coordination).

"International Workshop on Novel Quantum Phenomena in Transition Metal Oxides," Nov 22-24, 2004, AER (Maekawa Lab, Division of Advanced Research).

"1st Materials Science School for Young Scientists," Mar 3-5, 2005, Akiu.

10 Seminars by the IFCAM visiting professors.

2) Forums

Two forums, "Electronic Properties of Interfaces and Contacts" and "Electronic Properties of Molecular Assemblies," were set to exchange ideas on the important issues toward the future of material science. The first forum was an international one, held in Akiu on Nov 29-30.

I. Fukuyama Laboratory

【Research Activities】

Theoretical studies on the quantum properties of electrons in solids are pursued. Special targets this year are as follows;

(1) Electronic Properties of Molecular Assemblies.

Our studies on electronic properties of molecular solids so far, especially those of A_2B type

charge transfer salts, have been summarized in a review [**Ref.*2***]. At the same time new researches on typical examples of π-d systems, phthalocyanine and single component molecular metals, have been explored. As an interesting example of non-crystalline molecular solids, a possible mechanism of carrier doping into DNA has been clarified. [**Ref.*1***].

(2) Conductance of a Molecular Chain.

As a first step toward fundamental understanding of the possible molecular device, the length dependences of conductance of a finite molecular chain with contacts have been elucidated.

1. H.Kino, M.Tateno, M.Boero, J.A.Torres, T.Ohno, K.Terakura, H.Fukuyama
A Possible Origin of Carrier Doping into DNA
J. Phys. Soc. Jpn 73, 2089 (2004)

2. H.Seo, C.Hotta, H.Fukuyama
Toward Systematic Understanding of Diversity of Electronic Properties in Low- Dimensional Molecular Solids
Chemical Review 104, 5005 (2004)

II. Chen Laboratory

【Research Activities】

In the last fiscal year I have published 6 papers in international journals, including Science and Phy. Rev. B, and gave 1 invited talk in the international workshop, and 3 lectures. Additionally, I served as a board reviewer for **Matell. Mater. Trans. A**, and reviewer for **Nature Materials, APL, Scripta Mater.** and **Acta Mater**. One of my proposals (Science Research Fund (kaken-hi) A) has been awarded. In summary, I think I have a pretty good year as the starting point of my new career at Tohoku University.

1. **M. W. Chen** and X. Q. Yan
Comment on "Grain boundary mediated plasticity in nanocrystalline nickel"
Science, 2005, V308, p.5720

2.**M. W. Chen**, A. Inoue, T. Sakurai, E. S. K. Menon, R. Nagarajan, and I. Dutta
Redistributions of alloying elements in quasicrystallized Zr-Al-Ni-Cu-Ag bulk metallic glass
Phys. Rev. B, 2005, vol 71,p. 092202

3.K. A. Peterson, I, Dutta and **M.W. Chen**
Processing and characterization of diffusion-bonded AI-Si interface
J. Mater. Proc. Tech., 2004,Vol.145, 99.

4.Y. Ding, **M. W. Chen** and J. Erlebacher
Metallic Mesoporous Nanocomposite Materials for Electrocatalysis
J. Amer. Chem. Soc. 2004, vol 126, p. 6876

5.B. S. Xu, P.Han, J.Liang, X. G. Liu, H. Q. Bao, T. B. Li, M. W. Chen,
Theoretical investigation of the reflectivity of fullerene-(C-60, C-70)/AlN multilayers in UV region
SOLID STATE COMMUNICATIONS, 2005, Vol. 133, 353-356

6.M. L. Glynn, **M. W. Chen**, K. T. Ramesh, and K. J. Hemker
Influence of martensitic transformation on the stress development in thermal barrier coating systems
Mater. Metall. Trans., 2004, vol. 35A, 2279 (2004).

III. Inoue Project

【Research Activities】

Reported as following are the research activities of the Inoue Research Group in IFCAM, IMR, Tohoku University in 2004. The researches were mainly conducted by Prof. Alain Reza Yavari from Institut National Polytechnique de Grenoble, France during October 15, 2004 - January 14, 2004, and Prof. Walter Jose Botta Filho from Federal University of São Carlos, Federative Republic of Brazil during November 1, 2004 - January 31, 2005. As a result of their study, new findings have been obtained in the following aspects: nature of the free volume of metallic glasses, fabrication of Cu-based metallic glasses and their glass forming ability, hydrogen absorption composites as a energy material. The details of the results are described below with referring to the publication lists. <Publication List No. 1: Free Volume> It is widely accepted that in crystalline materials, lattice expansion as measured by diffraction methods differs from the expansion of the sample dimensions as measured by dilatometry. This difference is due to the contribution of thermal vacancies to the latter. We have found that in glassy materials and metallic glasses, however, this difference is not due to the contribution of free volume. These findings are regarded as the first direct experimental confirmation of simulation results indicating that atomic size holes are unstable in glasses such that free volume is dispersed randomly. This result can be used for the direct measurement of excess free volume in glasses using diffraction methods in place of dilatometry. < Publication List No. 2: Cu-based Glassy Alloys> A group of Cu-Ti-Zr-Ni-X (X = Fe, Si, Sn, Pb) bulk glassy alloys was produced by copper mold casting. The glass-forming ability (GFA) and the devitrification behavior of the glassy alloys were investigated by differential scanning calorimetry and synchrotron experiments. The GFA was evaluated by considering following indicators: the reduced glass transition temperature T-rg = T-g/T-1 (T-1 = liquidus temperature), the supercooled liquid region △T(x) = T-x - T-g, and a new parameter gamma defined as T-x/(T-g + T-1). The maximum values of the indicators are as follows: △T(x) = 57K for Cu47Ti33Zr11Ni8Si1, T-rg and gamma for the Cu47Ti33Zr11Ni8Fe1 and Cu47Ti33Zr11Ni8Si1, respectively. The comparison of the parameters indicates that T, and gamma correlate better with GFA than AT,. In situ recorded XRD scans reveal that the first crystallizing phase has a gamma-CuTi-type structure. The microstructure stable before melting contains a mixture of gamma-CuTi, Cu51Zr14, Cu2TiZr and Ti2Cu compounds. < Publication List No. 3: Energy Materials> It is reported that the development of new nanostructured MgH2 composites in which fluorine and TM catalysts are

introduced through the addition of TM fluorides such as FeF3. Subsequently, a fluorine transfer reaction takes place in the alloy, followed by the generation of protective MgF2 plus Fe nanoparticles catalyst. The powders thus obtained show sharply accelerated H-sorption kinetics at 300 degrees Celsius. In addition, hydrogen-sorption at rates applicable can be obtained at temperatures much lower than those reported for MgH2 with other catalysts without significant loss of capacity. < Publication List No. 4: Energy Materials> By employing mechanical alloying of nanograined MgH2 with addition of small amounts of FeF3 combined with a fluoride transfer reaction, a nanocomposite powder containing both the transition metal and fluorine as catalysts are produced. The solid-state phase transformations and microstructural changes during milling and/or during heating were studied by X-ray diffraction during in-situ heating, transmission electron microscopy, differential scanning calorimetry and magnetization measurements. The fluoride transfer reaction takes place partially during milling and can be completed during the first heating cycle. An improved hydrogen-desorption behavior was observed in such nanocomposite powder in comparison with the best reported values for MgH2-based composites. < Publication List No. 5: Free Volume> In order to clarify the relationships between the thermal expansion and relaxation of glassy materials, in situ transmission diffraction experiments were conducted using high-energy, high-intensity synchrotron light on heating for a pyrex glass. As a result, it is found that the evolution with temperature as well as time of the position of the first diffraction maximum of the diffraction pattern accurately reflects the thermal expansion coefficient and the relaxation behavior of the pyrex glass. This experimental result indicates that with diffraction experiments one can quantitatively determine the glass transition Tg, which is usually conducted with thermal analyses. In addition, the excess quenched-in free volume and its relaxation kinetics can also be determined by this technique.

1. "Excess free volume in metallic glasses measured by X-ray diffraction"
A.R. Yavari, A. LeMoulec, A. Inoue, N. Nishiyama, N. Lupu, E. Matsubara, W.J. Botta F., G. Vaughan, M. D. Michiel and A. Kvick
Acta Mater., 53 [6](2005), 1611-1619

2. "Glass formation and crystallization of CU47Ti33Zr11Ni8X1 (X = Fe, Si, Sn, Pb) alloys"
M. Calin, M. Stoica, J. Eckert, A.R. Yavari and L. Schultz
Materials Science and Engineering A-Structural Materials Properties Microstructure and Processing, 392 [1-2](2005), 169-178

3. "Improvement in H-sorption kinetics of MgH2 powders by using Fe nanoparticles generated by reactive FeF3 addition"
A.R. Yavari, A. LeMoulec, F.R. de Castro, S. Deledda, O. Friedrichs, W.J. Botta F., G. Vaughan, T. Klassen, A. Fernandez and A. Kvick
Scripta Mater., 52 [8](2005), 719-724

4. "Improving H-sorption in MgH2 powders by addition of nanoparticles of transition metal fluoride catalysts and mechanical alloying"
J.F.R. de Castro, A.R. Yavari, A. LeMoulec, T.T. Ishikawa and W.J. Botta F.

J. Alloys Comp. 389 [1-2] (2005), 270-274

5. "Glass transition T-g, thermal expansion, and quenched-in free volume Delta V-f in pyrex glass measured by time-resolved X-ray diffraction "
K. Ota, W.J. Botta F., G. Vaughan and A.R. Yavari
J. Alloys Comp., 388 [1](2005), L1-L3

【Plan】

During the research periods in Inoue Research Group in IFCAM, IMR, Tohoku University, Prof. Yavari and Prof. Botta are partially cooperated, and going to conduct their study the characteristics of the non-equilibrium materials, such as metallic glasses and nano-scale particles. Prof. Yavari is planning to study the following two research topics: (1) clarification of the characteristics of the free volume in metallic glasses through diffraction experiments, and (2) fabrication of the novel metallic glasses. As for the first topic, Prof. Yavari is going to measure the glass transition temperature by the experimental results using Synchrotron radiation, which is a strong contrast to the conventional technique with thermal analyses. The thermal expansion and relaxation of glassy materials are focused on, and their relationships to glass transition phenomenon will be studied. The research on the second topic will be made for Cu-based glassy alloys and their glass forming ability will be evaluated. The reason for selecting Cu-based glassy alloys is that only a few Cu-based glassy alloys have been found to date because of the difficulty of fabrication as a glassy alloy, although Cu-based alloys are one of the practical metallic materials. In addition, and the mechanism of formation as a glassy materials has not yet been clarified for Cu-based glassy alloys. As for the evaluation of the glass forming ability, the reduced glass transition temperature denoted by Trg, which is obtainable by normalizing the glass transition temperature by its liquidus temperature, is going to be adopted for the Cu-based glassy alloys which will be obtained in this research. The Trg is supposed to be compared with that for typical glassy alloys, and by summarizing the difference of the tendency of the glass forming ability, the mechanism of formation of Cu-based glassy alloys will be derived.

Prof. Botta Filho is going to make his research on fabricating the hydrogen absorption metallic materials in Mg-based alloys with cooperation of Prof. Yavari. As target materials, MgH2 in nanometer-scale powder shape will be prepared, and hydrogen sorption behavior of the powder will be studied. In preparing alloys, some kinds of solid-reaction, a fluoride transfer reaction combined with a reaction due to mechanical alloying, will be utilized in this fabrication of the powders. After preparing the powder specimens, the precise analyses will be conducted for the alloys thus obtained with respect to structure, morphology, thermal stability and magnetic properties using transmission electron microscopy, differential scanning calorimetry and magnetization measurements. The applicability of the MgH2 powders also will be evaluated in this research by comparing to the characteristics of the MgH2 reported previously with respect to the temperature at which H-sorption rates are acceptable for applications.

IV. Sakurai Project

【Research Activities&Plan】

In academic year 2004, Dr. Nagao's group continued the STM/LEEM investigation of the thin film Bi growth on the Si (111)-7x7 surface to elucidate the mechanism of coverage-dependent phase transition of the Bi ultra-thin film. We concluded with the help of theory group in NIMS that the Bi film has a unique new phase, stable up to the film thickness of 4 monolayers. The bonding configuration of this phase is similar to black phosphorus which belongs to the same elemental group as Bi, but has been never observed in bulk Bi. (**Ref. *1***) We hope that this new allotrope of Bi may possibly be accompanied with exotic electronic properties, realizing unique Bi properties. We plan to investigate it in the coming year, although Dr. Nagao left our group in September 2004 to take a position at NIMS, Tsukuba.

The main thrust of our group for last couple of years is Ge (105)/Si project mainly performed by Dr. Fujikawa and his students. Realizing its rather complicated nature of the surface structure due to large charge transfer, they used high-performance atomic force microscopy (AFM) to nail down the details of its atomic structure in collaboration with Dr. Hasegawa's group at ISSP, University of Tokyo. (**Ref. *2***). They found that the obtained AFM images documented the exact positions of the dangling bonds on the surface with the resolution even higher than the best STM images currently available. Furthermore, using the Kelvin force microscopy together with the AFM, an atomically-resolved potential map was successfully resolved on the surface, which renders additional support to the structure model which we propose. To our best knowledge, this is the first atomically resolved potential mapping obtained using this unique technique. These results nicely exemplify the power and usefulness of AFM in surface structure. This research was extended to further investigate hydrogen adsorption and they have found that the surface strain on this surface is controllable by the hydrogen adsorption. (PRL 94, 086105 (2005).) This work implies the possibility of strain control of Ge quantum dots on Si through adsorption. Use of "surface strain" as a controllable parameter in surface engineering will be our major area of research for the coming years. For instance, we plan to investigate in what degree we can modify the strain in the Ge films and nanostructures by adsorption in order to control mechanic and electronic properties of the Ge/Si sytem.

Highly challenging "growth of GaN on Si" was attempted by Dr. Yamada-Takamura's group using the UHV molecular beam epitaxy (MBE)–SPM system. GaN is grown on Si (111) by radio-frequency plasma-assisted MBE, and the growth front is studied using reflection high-energy electron diffraction (RHEED) and STM. By successfully documenting the optimum nucleation/growth conditions, well-defined surface reconstructions, i. e. GaN-(000-1)-3x3, 6x6, and c(6x12), are observed by STM after the additional Ga deposition at R.T., indicating the uniform N-polarity of the grown film. They have concluded that the initial GaN nucleation under N-rich conditions is crucial in order to grow mono-polar uniform GaN films on the Si substrate. (APL in press (2005)). We currently extend this GaN/Si system research to include ZrB_2 buffer layer for better GaN film growth. We also plan to study diamond surfaces by UHV non-contact-AFM.

Dr. Wu worked successfully to document the two dimensional nature of alkali metal adsorbate

on the Si (111)-7x7 surface at low coverage and formation of magic cluster upon the critical coverage of 4 atoms/unit cell.. This work was further augmented by low-temperature STM study to control the movements of alkali-metal atoms on the surface. These results were in complete agreement with the theoretical potential mapping and computer simulation of STM data by Kawazoe-Lab. (**Ref. *3***) Dr. Wu left our group to take up a professorship at Institute of Physics, Chinese Academy of Sciences, Beijing in January 2005.

Halogen (Cl, F) etching of the GaN (000$\pm$1) surface is being continuously studied in connection to its technological importance in device fabrication process by Dr. Fujikawa's group. This work is part of S. Kuwano's Ph.D. thesis research. They found, among others, that the Ga-rich condition is essential to efficient etching of the GaN surface using chlorine. (**Ref. *4***)

In LEEM/STM study by Dr. Sadowski's group, well ordered bismuth films on Si (111) were used as templates for the growth of thin organic films of pentacene. Making a good use of low-energy electron microscopy (LEEM) and STM, they found that pentacene nucleates on the Bi (001) substrate into a highly ordered, bulk-like crystalline layer, with the molecules "standing up" on the Bi surface, with the (001) plane as the growth front. Moreover, the Pn layer is aligned epitaxially with the Bi (001) surface having a "point-on-line" commensurate relation with the substrate, which is the first report on the epitaxial growth of pentacene. It was also found that the Pn/Bi (001) film crystallizes in the bulk-like structure directly from the first Pn layer, and that the diameter of the first-layer Pn islands exceeds as much as 200 μm, one of the largest pentacene islands reported up to date. (APL 86, 073109 (2005)) As an ongoing joint work with Professor Nakajima's group in this area, perylene-3.4.9.10-tetracarboxylic dianhydride (PTCDA) thin film grown on the hydrogen-terminated, vicinal Si (111) substrate was investigated by UHV STM, and the possible adsorption model has been proposed, in which the long axis of the 2D unit cell of PTCDA matches the vector (6, 2) of the H-Si(111) surface, and PTCDA lattice has a point-on-line coincidence with the H-Si (111) lattice. (**Re. *5***) fIn the coming year we plan to extend our activities onto studying the growth mode, crystallographic and electronic transport properties of other organic thin films, such as perfluoropentacene, pentacene-quinone and rubrene.

We also note profitable collaboration in various research with Professor Chen's group at IFCAM.

References

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"Nanofilm allotrope and phase transformation of ultrathin Bi film on Si (111)-7x7,"
Phys. Rev. Lett. 93, 105501 (2004).

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"Imaging of All Dangling Bonds and Their Potential on the Ge/Si (105) Surface by Noncontact Atomic Force Microscopy,"
Phys. Rev. Lett. 93, 266102 (2004).

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Kawazoe, R. F. Dou, Q. K. Xue and T. Sakurai,
"Step-by-step cooling of a two-dimensional Na gas on the Si (111)-(7x7) surface,"
Phys. Rev. B70, 195417 (2004).

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"Bilayer-by-bilayer etching of 6H-GaN (0001) with Cl,"
Surf. Sci. 561, L213 (2004).

5. G. Sazaki, T. Fujino, J. T. Sadowski, N. Usami, T. Ujihara, K. Fujiwara, Y. Takahashi, E. Matsubara, T. Sakurai, and K. Nakajima
Epitaxial relation and island growth of perylene-3.4.9.10-tetracarboxylic dianhydride (PTCDA) thin film crystals on a hydrogen-terminated Si (111) substrate,"
J. of Crystal Growth 262, 196 (2004).

V. Maekawa Project

【Research Activities】

In this project, novel quantum phenomena in advanced materials and nanostructures are theoretically studied. In 2004, the following two topics were the main subjects for the research:

（1） Spin dependent transport in magnetic nanostructures:

In nanostructures with ferromagnet and superconductor, spin current causes novel quantum phenomena. This is because in a superconductor, spin and charge propagate independently. Some of such nano-devices were proposed (***1,2,3***). A new superconducting computing device (qubit) consisting of Josephson devices with a ferromagnet was also examined.

（2） Transition metal oxides as materials for future electronics devices:

Transition metal oxides are expected to be materials for the future electronic devices and environmental ones. However, a variety of problems in the electronic states remain to be solved. In order to explain the basic physics in transition metal oxides and discuss the recent progress in the research, a textbook entitled “Physics of Transition Metal Oxides” has been published from Springer Publisher (Germany) (***5***). The orbital degree of freedom of electrons, which controls the electronic properties, was considered to be a hidden parameter in the oxides, since the method of direct observation was not known. Here, a theory of the observation of orbital and its excitations by using the synchrotron radiation has been proposed and applied to the experiments (***4***).

1. S. Maekawa:
Spin-dependent transport in magnetic nanostructures.
J. Mag. Mag. Matr. **272-276** (2004), E1459-E1463

2. S. Takahashi and S. Maekawa:
Spin injection and detection in F/N/F and F/S/F nanostructures.
J. Mag. Mag. Matr. **272-276** (2004), E1423-E1424

3. M. Ichimura, S. Takahashi, K. Ito, and S. Maekawa:
Geometrical effect on spin current in magnetic nanostructures.
J. Appl . Phys. **95** (2004), 7255-7257

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Resonant inelastic x-ray scattering study of the hole-doped manganites $La_{1-x}Sr_xMnO_3$ (x = 0.2, 0.4).
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