Workshop in 2015

The 7th Materials Information, Characterization, and Exploration (MICE-7)

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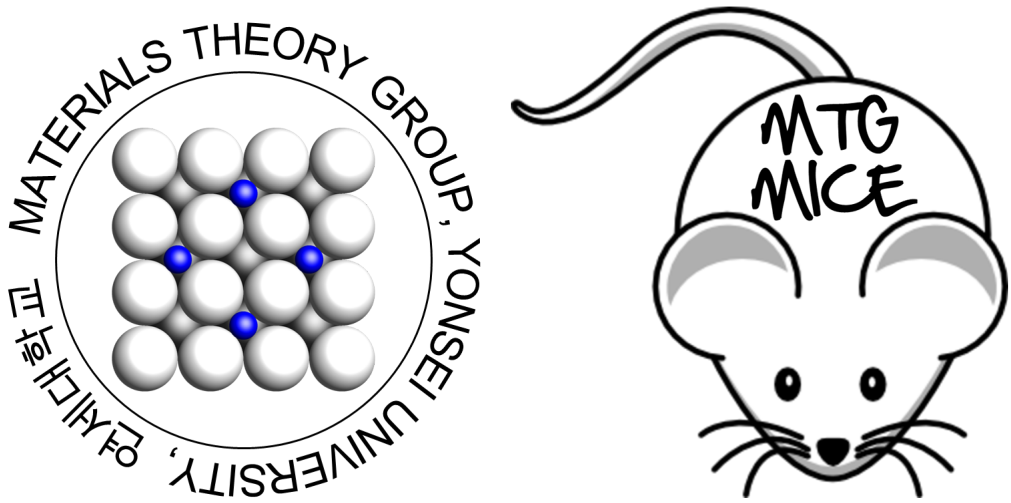

Organized by Materials Theory Group, Yonsei University, Korea

Content page & Schedule

[Characterization Session]

Energetics of various stoichiometries of titanium nitrides and formation of point defects: First-principles study

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Titanium nitride is a robust material which has high performances for various technological applications. It is known that nitrogen vacancies, V_N are regarded as the primary defects that control the composition ratio of sub-stoichiometric TiN [1]. However, the effect of nitrogen condition to the TiN system still remains an open question. According to this curiosity, I studied predicted structures of Ti_xN_y in N-lean or N-rich condition. In the paper by V. Ivashchenko *et al.* [2], they suggest stable or meta-stable phases of Ti_2N which can be represented in anatase, anti-rutile, and Cd_2I-type Ti_2N structures. On the other hands, the paper written by P. Kroll [3] revealed various structures of Ti_3N_4. (*e.g.* $CaTi_2O_4$-type, Zr_3N_4-type, and Th_3P_4-type) Most recently, S. Yu *et al.* [4] suggested other stoichiometries of Ti_xN_y with convex-hull diagram. With the suggested structures from the papers, we present density-functional theory (DFT) study of the relative stabilities according to different growth conditions. Additionally, the formation energies of point defects of each stoichiometry were studied.

[1] Z. Dridi *et al.*, *J. Phys.-Condens. Mat.* **14** 10237 (2002)

[2] V. Ivashchenko *et al.*, *Phys. Rev. B* **86**, 064109 (2012)

[3] P. Kroll, *Phys. Rev. Lett.* **90**, 125501 (2003)

[4] S. Yu *et al.*, *Phys. Chem. Chem. Phys.* **17**, 11763 (2015)

[Characterization Session]

The influence of van der waals corrected exchange correlation functional on Elastisity

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Current materials-related calculations employ the density-functional theory (DFT), commonly using approximations for the exchange-correlation (xc) functional. However this (semi-)local and hybrid functional suffer from the self-interaction error and lack the long-range van der Waals (vdW) energy tail. To asses the role of vdW interaction in solid, we employ DFT calculation with recently developed vdW-corrections (Gimme's D scheme, Tkatchenko-Scheffler (TS) scheme, as well as non-local correlation vdW-DF functional of Langreth and Lundqvist *et al.*) based on generalized gradient approximation as exchange functional. In this work we study the influence of vdW corrected exchange correlation functionals on the elastic properties, Elastic constnats (C_{ij}) Bulk modulus(B_0), Young's Modulus (E_{hkl}) etc. The properties in isotropic constants shows a general trend following the one in cohesive energy. But the anisotropic analysis show that PBE with TS with self-consistently screened (SCS) scheme shows a drastic changes. Based on these analysis, we could get an description of vdW interaction not only in isotropic bulk, but in anisotropic properties, which is highlighted in nano-size technique and low-dimensional systems.

[Characterization Session]

Introducing Myself

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For upcoming summer Materials Information, Characterization, and Exploration (MICE) workshop in 2015, I will introduce my self with various contents. First of all, a brief introduction of who I am will be represented, for example, age or hobby. Secondly, the desire to study somethings from the basics with the strong theoretical background are presented in detail, as a main reason why I apply Materials Theory Group (MTG). Finally, my interest for modeling the process and computational nanotechnology are shown based on two articles that caught my eyes during the last 2 weeks of internship. The first one is 'Low barrier carbon induced CO dissociation on stepped Cu' introduced at the last week's student meeting [1]. This surprised me that the computational method can be used for expecting the graphene making process. On the other hand, the Nonstoichiometric Nucleation and Growth of Multicomponent nanocrystals in Solution' within MTG publication list also impressed me because the computational method is used for expecting or modeling the atomic level area and it is related to the real experiments [2].

[1] Y. Min, J. Kwak, A. Soon, *et al., Acc. Chem. Res.* **47**, 2887 (2014)

[2] M. Ng, F. Abild–Pedersen, S. Kaya, *et al., Phys. Rev. Lett.* **114**, 246101 (2015)

[Characterization Session]

Surface oxide effect on the adsorption of PMDA-ODA on Cu(111)

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In this new age of flexible electronics, highly durable (and yet flexible) printed circuit boards (PCBs) are especially critical to the operation of such bendable electronic devices. From a materials perspective, the adhesive properties of the aromatic polyimide layer to the metal surface very much determines the overall long-term performance of such devices [1]. Given its high mechanical strength, and thermal and chemical resistance, poly(pyromellitic dianhydride oxydianiline) (PMDA-ODA) has been the choice polymeric substrate for the copper in these flexible PCBs [2]. To date, the poor adhesion in PMDA-ODA/Cu hybrid-interface has led to the limitations of its use as flexible and bendable PCB materials [3]. Despite of the significant demands for the improvement of PMDA-ODA/Cu hybrid-interface, there is still no clear principle for the early stage of the adsorption of organic film on metal surface. In this work, using first-principles density-functional theory (including van der Waals corrections), we study the fundamental physio-chemical properties of the molecular fragments of PMDA-ODA on both pristine Cu(111), as well as oxidic O/Cu(111). Our results may pave the road to explore this hybrid-interface by offering an increase understanding of the physio-chemical reaction on metal surface.

[1] B. Noh, J. Yoon, and S. Jung, *Int. J. Adhes. Adhes.* **30**, 30 (2010)

[2] Y. Takagi, Y. Gunjo, H. Toyoda , and H. Sugai, *Vacuum* **83**, 501 (2009)

[3] R. Saraf, J. Roldan, and T. Derderian, *IBM J. Res. Dev.* **38**, 441 (1994)

[Characterization Session]

Effect of halogen ion on TiN surface

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Platinum is one of the most broadly used catalyst for many chemical reactions (e.g. oxygen reduction reaction). Although its great reactivity, platinum catalysis has not met enthusiastic reception from industry due to its high price. Pt/C catalyst is widely used to come over this problem, but still considered as an imperfect solution because of its poor stability [1,2]. Recently, platinum single-atom catalyst with TiN support has suggested and proved to be stable on the N vacancy site of TiN support under N-lean condition [3]. For synthesis of Pt single atom catalyst, precursor which containing Cl is widely using these days (e.g. $Pt(NH_3)_4Cl_2$) and possibility of residual Cl ion on Pt single atom catalyst system is exists. In this work, we present density-functional theory (DFT) study of the influence of chlorine ion on TiN surface. From here, we will discuss possibility of residual chlorine ion on TiN surface and how it will influence to Pt/TiN single-atom catalyst system.

[1] Z. Peng and H. Yang, *Nano Today* **4** 143 (2009)

[2] B. Avasarala, T. Murray, W. Li and P. Haldar, *J. Mater. Chem.* **19** 1803 (2009)

[3] R. Q. Zhang, T. H. Lee, B. D. Yu, C. Stampfl and A. Soon, *Phys. Chem. Chem. Phys.* **14** 16552 (2012)

[4] T. J. Schmidt, U. A. Paulus, H. A. Gasteiger and R. J. Behm, *J. Electroanal. Chem.* **508** 41 (2001)

[Intern Session]

Nice to meet MTG

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It's been a few weeks after I joined Materials Theory Group (MTG) as an intern student of 2015 summer vacation. As the member of Yonsei Energy & Environmental Economics forum (YEEF), I became interested in the substances which occurs environment pollution (e.g. UO_2). And, inspired by my previous major, aerospace material engineering, I also have interests about aerospace materials (e.g. metallic glass composite). In this talk, I want to share my research interests, which are mentioned above. Additionally, I also want to talk about who am I, why I choose MTG and what I want to get from MTG. I hope that from this talk, we can understand more about each other and have meaningful discussion about my research interests.

[1] Hun Bok Jung *et al.*, *Environ. Sci. Technol.* **46** 7301 (2012)

[2] P. Maldonado *et al.*, *J. Phys. Chem. C* **118**, 8491 (2014)

[Characterization Session]

Theoretical X-ray absorption spectroscopy and case studies

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Experimental study of core level spectroscopy has made remarkable progress using third-generation synchrotron radiation sources. Among them, x-ray absorption spectroscopy (XAS) is widely used technique for determining the local geometric and electronic structure of matter. It has element selectivity, because each element on the periodic table has a set of unique absorption edges corresponding to different binding energies of its electrons. Also it is phase independent, so samples can be in the gas-phase, solution, or solids. Currently, interpretation of experimental XAS is commonly achieved by fingerprinting, that is, comparison to known standards or their linear superposition. In this talk, we will discuss how theoretically simulated XAS will be achieved and used as standards for experimental XAS results. Several cases will be studied which include comparison between theoretical and experimental XAS, especially using multiX code [1].

[1] B. Delley, *et al., Phys. Rev. B* **85**, 125133 (2012)

[Characterization Session]

Electronic structure modification of black phosphorus mediated by dimensionality and deformation: An *ab initio* study

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By using first-principles calculations, we tried to handle both dimension and controllable structural distortion starting from bulk black phosphorus. In the dimensional point-of-view, we considered low-dimensional phosphorus ranging from two-dimensional phosphorene to one-dimensional phoshporene nanoribbon, and in terms of controllable distortion, we selected line defect for two-dimension case and twisting for one-dimension case. Based on density-functional theory (DFT), we investigated the change of thermodynamic stability and electronic structure. In this study, we found that the energies can be stored in the 1D phosphorene nanoribbon (PNR) by giving a structural distortion, and also the change of electronic band gap was observed. For the 1.5D phosphorene nanoribbon, defected structures have showed very low defect formation energy and different electronic structure, implying the possibility of modification of electronic structure by adopting line defect in the structure.

[1] E. S. Reich, *Nature* **506**, 19 (2014)

[2] L. Li, *et al., Nat. Nanotechnol.* **9**, 372 (2014)

[3] H. Liu, *et al., ACS Nano* **8**, 4033 (2014)

[4] Y. Liu, *et al., Nano Lett.* **14**, 6782 (2014)

[Intern Session]

Research Suggestion for Enhancing Humidity Resistance of Perovskite Solar Cells

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In this workshop, I am planning to share some my personal experiences. After that, some talks will be followed including motivation which made me to apply in MTG. Lastly, there will be a brief introduction for my research plan about renewable energy, especially for solar cells.

Recently, many people are focusing on perovskite solar cells (PSCs) because of their drastically increased power conversion efficiency compared to classical solar cells [1]. However, PSCs have crucial difficulties since they have high chance of decomposition in working environment [2]. Especially, low resistance for humidity is the most important drawback because operating ability of solar cell in humid environment is necessary for its applications. However, reported solutions are imperfect so that some additional problems are occurred [3,4]. Therefore, during internship program period, I am planning to apply computational methods on typical perovskite structures to study the basic properties and develop some alternative solutions to improve humidity resistance of PSCs.

[1] M. A. Green *et al., Nat. Photonics* **8**, 506 (2014)

[2] G. Niu *et al., J. Mater. Chem. A.* **3**, 8970 (2015)

[3] X. Dong *et al., J. Mater. Chem. A.* **3**, 5360 (2015)

[4] I. C. Smith *et al., Angew. Chem. Int. Ed.* **53**, 11232 (2014)

[Intern Session]

Electronic properties of single-strand polyimides

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Bulk heterojunction (BHJ) blends of conjugated polymers with fullerene derivatives are one of promising type of organic photovoltaic (OPV) cells because of their high efficiency, ambipolar transport properties and solution processability [1-2]. However, their stability to environment is one of main bottlenecks to commercialize. Meanwhile, polyimides (PIs) have been broadly used polymer due to their excellent mechanical strength, high thermal stability, and good resistivity to chemicals and radiations [3]. In this work, we present density-functional theory (DFT) study to investigate suitability of PIs as a donor material for BHJ OPV cells. By analyzing the elelctronic properties of selected PIs, we not only check possibility of PIs as a electron donor but also predict which PI among selected PIs will be efficient.

[1] N. S. Sariciftci, L. Smilowitz, A. J. Heeger, and F. Wudl, *Science* **258**, 1474 (1992)

[2] C. J. Brabec, S. Gowrisanker, J. J. M. Halls, D. Laird, S. Jia, and S. P. Williams, *Adv. Mater.* **22**, 3839 (2010)

[3] M. K. Ghosh and K. L. Mittal, *Polyimides: Fundamentals and Applications* (Dekker, New York, 1996)

[Characterization Session]

A first-principles investigation of Sn/Cu(001)

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Layer deposition of Sn on Cu(001) can give rise to a rich variety of surface reconstructions in the submonolayer to high surface coverage range of Sn [1]. To date, the explicit atomic geometry of high surface coverage structure of Sn/Cu(001) is still strongly debated. Thus, using density-functional theory coupled with the ab initio atomistic thermodynamics approach [2,3], we attempt to map out the ab initio surface phase diagram of the Sn/Cu(001) system, hopefully providing insight into the rich surface chemistry of this near-surface alloy system. In particular, we will present the binding energies, electronic structure (i.e. work function and simulated scanning tunneling microscope images [4]), and the atomic geometries of various interesting surface reconstructions of Sn on Cu(001) as a function of Sn surface coverage.

[1] M. Lahti, K. Pussi, E. McLoughlin, and A. A. Cafolla, *et al., Surf. Sci.* **605**, 1000 (2011)

[2] M. Scheffler and J. Dabrowsk, *Philos. Mag. A* **107**, 58 (1988)

[3] K. Reuter and M. Scheffler, *Phys. Rev. B* **65**, 035406 (2001)

[4] J. Tersoff and D. R. Hamann, *Phys. Rev. B* **31**, 805 (1985)

[Characterization Session]

Oxygen adsorption and stability of copper surface oxides on the (111) surface of gold: A theoretical surface science approach

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Ultrathin oxide layers grown on metal substrates are proposed to be a new class of materials with remarkable properties [1]. Various oxides of copper are of interest for heterogeneous catalysis and were previously proposed as outstanding catalysts for the watergasshift reaction, NO_x reduction, and methanol synthesis from syngas [2]. Recently, via reactive Cu deposition in an oxygen ambience, high crystallographic quality of the cuprous oxide (Cu_2O) thin films on gold support have been prepared [3]. However, the exact atomic structure of thin film-like Cu_2O, which depends on the oxygen environment, is still under debate.

In this work, we perform density-functional theory (DFT) calculations using the Vienna *ab initio* Simulation Package in combination with *ab initio* atomistic thermodynamics to investigate stability of Cu_2O thin films on Au(111) as a function of oxygen chemical potential. Our results indeed show that some of the surface structures suggested in Ref. [3] are energetically more stable than the traditional copper oxide thin film structures on copper substrate. Our results provide a preliminary theoretical basis to pursue further studies of these complex surface oxidic layers on metal substrate.

[1] C. Freysoldt et al., *Phys. Rev. Lett.* **99**, 086101 (2007)

[2] T. Schedel-Niedrig et al., *Phys. Chem. Chem. Phys.* **2**, 3473 (2000)

[3] H. Strater et al., *J. Phys. Chem. C* **119**, 5975 (2015)

[Intern Session]

Research outlook of Yunjae in MTG

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I would like to highlight following things in this talk: (1) research interests via cutting-edge quantum mechanics based on computational simulation; (2) abilities to be grown as well-educated international level researcher under firm disciplines of materials theory group (MTG). In MTG, using first-principles calculation, physical and chemical properties of diverse materials will be investigated. Firstly, based on understanding of Schrödinger equation, so called, properties of diverse nano-structured materials, e.g. quantum dots, thin films, and 2D materials will be studied. Also, practical applications of these diverse nano-structured materials will be found using computational simulations in a range of fields, e.g. physical, chemical, biological, and medical engineering. One of my strength is the positive mindset not to surrender easily to scientific problems. To be a well-educated international level researcher, the heartbeat, lab, product, and network are compulsory from professor's saying. To grow these mindsets and skillset, I will be a synergetic collaborator with lab members and passionate learner.

Erwin Schrödinger, novel price winner, said "If you cannot tell everyone what you have been doing, your doing has been worthless." To make my effort and time valuable, I'll do my best in research activity. When I complete research project, I hope to present my research results to everyone confidently.