

Monday Afternoon, December 8, 2014

Thin Films

Room: Lehua - Session TF+NM-MoE

Nanostructures, Graphene, and Magnetism

Moderator: Stephen Muhl, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México

5:40pm **TF+NM-MoE1 Low-Dimensional Electronic System on Metal-Adsorbed Germanium Surfaces**, *Kan Nakatsuji*, Tokyo Institute of Technology, Japan **INVITED**

The electronic properties of metallic nano-materials attract much interests not only because of their potential application to novel electronic devices but fundamental low-dimensional physics point of view. One of the ways to fabricate nano-materials is to deposit small amount of metal atoms on crystalline semiconductor surfaces. In the present study, we have investigated atomic and electronic structures of gold adsorbed Ge(001) and Ge(111) surfaces which exhibit one- and two-dimensional atomic structure, respectively, by scanning tunneling microscopy (STM), angle-resolved photoelectron spectroscopy (ARPES) and density functional calculations.

The Au-adsorbed Ge(001) surface has periodic arrangement of one-dimensional (1D) chain structure and a metallic surface state. This metallic state has been reported to be strictly 1D showing Tomonaga-Luttinger liquid (TLL) behavior[1]. In the present study, its band shape was precisely investigated using a single-domain surface prepared on a vicinal substrate. Our ARPES results clearly revealed that the band has anisotropic two-dimensional (2D) shape in contrast to the previous report. The band dispersion is steeper in the direction perpendicular to the chain contrary to the intuitive expectation from 1D structure[2]. Our STM study revealed that the top of the 1D chain shows 8 times periodicity on average along the chain with a lot of defects[3]. This rather high density of defects may cause the reduction of density of states at the Fermi level which was previously interpreted as a TLL behavior.

The Au-adsorbed Ge(111) surface exhibits $\sqrt{3}\times\sqrt{3}$ periodicity. Two metallic surface states, S_1 and S_2 , were observed around Γ , which is consistent with the calculated band structure of the CHCT model. 2D electronic system is confirmed by a rounded hexagonal Fermi surface of S_1 band[4] which has contributions from surface Au and Ge atoms. S_2 is originated only from the Ge atoms. These surface bands split into spin-polarized bands owing to the strong spin-orbit interaction[5]. The modification of the electron filling of the S_1 band by additional Au atoms will be also discussed[6].

The author thanks Y. Motomura, R. Niikura and Prof. F. Komori in Institute for Solid State Physics, University of Tokyo for their close collaboration, and Y. Oda and Prof. A. Ishii in Tottori University for their collaboration in theoretical part of this work.

- [1] C. Blumenstein et al., Nature Physics 7 (2011) 776.
- [2] K. Nakatsuji et al., PRB 84 (2011) 115411.
- [3] R. Niikura et al., PRB 83 (2011) 035311.
- [4] K. Nakatsuji et al., PRB 80 (2009) 081406@.
- [5] K. Nakatsuji et al., PRB 84 (2011) 035436.
- [6] K. Nakatsuji et al., JPCM 25 (2013) 045007.

6:20pm **TF+NM-MoE3 Effective Mass of a Two-Dimensional $\sqrt{3}\times\sqrt{3}$ Ga Single Atomic Layer on Si(111)**, *Michael Schnedler*, Forschungszentrum Jülich GmbH, Germany, *Y. Jiang*, Peking University, China, *K.H. Wu*, Institute of Physics, Chinese Academy of Sciences, China, *E.G. Wang*, Peking University, China, *R.E. Dunin-Borkowski*, *P. Ebert*, Forschungszentrum Jülich GmbH, Germany

The transport of charge carriers in semiconductor nanostructures is particularly important for nanoscale devices. In a semi classical approach, the transport of charge carriers is to a large degree governed by the effective masses of electrons and holes, which are reasonably well known for most bulk materials. However, with ongoing miniaturization of semiconductor devices and the trend towards the use of nanostructures, the increasing surface to volume ratio reduces the relative fraction of bulk material. Hence, transport in semiconductor nanostructures is to a large degree determined by surface and/or interface effects, where little is known about the effective masses.

The effective masses of surface states can be derived from angle-resolved photoemission spectroscopy (ARPES), but it is hardly applicable on individual nanostructures. In contrast scanning tunneling spectroscopy (STS) is ideally suited for probing the local density of states of an individual nanostructure, but it is a very difficult task to quantitatively

measure the involved k vectors and hence the dispersion relation and the effective mass.

Therefore, we illustrate here a methodology applicable to individual semiconducting nanostructures for extracting effective masses of a two dimensional $\sqrt{3}\times\sqrt{3}$ Ga single atomic layer on Si(111) directly from scanning tunneling spectra. The methodology is based on calculating the tunnel current using its dependence on the effective density of states mass and a parabolic band approximation followed by fitting to the measured tunneling spectra. An effective mass of $m_{\text{eff}}=0.59 \pm 0.06$ is obtained for the empty surface state, in good agreement with a band structure calculation and inverse photo electron spectroscopy data.

6:40pm **TF+NM-MoE4 α' , α'' -Fe₁₆N₂ Interstitial Compound as a New Candidate for Rare Earth Free Permanent Magnet - From Thin Film to Bulk**, *M. Takahashi*, *Masahiro Tobise*, Tohoku University, Japan **INVITED**

After surprising first report (α'' -Fe₁₆N₂ phase exhibited a giant saturation magnetization in 1972 as a thin film form [1]), many researches challenged to realize single phase α'' -Fe₁₆N₂. At 1993, present author et al. established the method in thin film to attain a relatively high volume fraction of α'' -Fe₁₆N₂ using a reactive sputtering [2]. Precisely determined value of M_s of ≈ 240 emu/g (≈ 2.2 T) even though relatively small value compared to initially reported one and value of K_u ($\approx 10^7$ erg/cm³) are very attractive as rare earth free permanent magnet material [3]. But as it was very difficult to form metastable α'' -Fe₁₆N₂ single phase even in the thin film, it had been believed that the synthesis of a single phase α'' -Fe₁₆N₂ in bulk form was almost impossible. In 2013, our group established the synthesis procedure of single-phase α'' -Fe₁₆N₂ nanoparticle for the first time, and reported α'' -Fe₁₆N₂ exhibit M_s of ≈ 234 emu/g and K_u of $\approx 10^7$ erg/cm³ [4]. This nanoparticle powder could be synthesized starting from the reduction of Fe-oxides and following nitriding with ammonia gas at temperatures around 145 °C under the very low moisture and oxygen contents less than 1 ppm through the all process. Mössbauer spectra also revealed that the perfect formation of the single phase α'' -Fe₁₆N₂. In order to improve coercivity through the evaluation of magnetic interaction and the quality of α'' -Fe₁₆N₂ crystalline, the anisotropy field H_i^{pfc} and switching field H_p are determined by rotational hysteresis loss analysis using randomly oriented nanoparticles assembly. Coercivity of nanoparticle assembly consisting of single-phase α'' -Fe₁₆N₂ formed around 145 °C exceeds 2000 Oe. Normalized coercive force H_c/H_i^{pfc} and normalized switching field H_p/H_i^{pfc} are about 0.16 and 0.3, respectively. Coercivity has been improved by surface treatment and reached 3200 Oe at present. Detail on the relationship between these magnetic properties and reversal mechanism is discussed.

References

- [1] T.K.Kim and M.Takahashi, Appl. Phys. Lett. 20, (1972) 492.
- [2] M.Takahashi, H.Shoji, H.Takahashi and T.Wakiyama, IEEE Trans.Mag.29 (1993) 3040
- [3] M.Takahashi and H.Shoji, J. Magn. Mater., 208, (2000) 145.
- [4] T.Ogawa, Y.Ogata, R.Gallage, N.Kobayashi, N.Hayashi, Y.Kusano, S.Yamamoto, K.Kohara, M.Doi, M.Takano and M.Takahashi, Appl. Phys. Express, 6 (2013) 073007

7:40pm **TF+NM-MoE7 Interfaces between Transferred, CVD-Grown Graphene and MoS₂ Probed with STM and ARPES**, *H. Coy-Diaz*, Department of Physics, University of South Florida, Tampa, FL 33620, USA, *J. Avila*, *M.C. Asensio*, 2. Synchrotron Soleil, Orme des Merisiers - Saint Aubin, BP 48 - 91192 - GIF SUR YVETTE Cedex, France, *Matthias Batzill*, Department of Physics, University of South Florida, Tampa, FL 33620, USA

Heterostructures made of different van der Waals materials are of increasing interest because of potential applications in energy harvesting and combination of spin- and valley-tronics. However, the interface properties of these materials are not yet well characterized. One challenge for their characterization is the preparation of large-area high quality materials that enable employment of surface characterization techniques such as scanning probe microscopy and photoemission spectroscopy. Here we demonstrate the transfer of CVD-grown graphene to bulk MoS₂ substrates and report the first STM and ARPES studies of such a system. As expected for weakly interacting materials STM studies only exhibit a very weak moire-superstructure and (nano) ARPES measurements show that the Dirac cone of graphene is maintained. However, (nano) ARPES also shows the formation of band-gaps in the pi-band of graphene where the out-of-plane molecular orbitals of MoS₂ intersect with the electronic-states of graphene. This modification of the electronic structure of graphene in the

graphene/MoS₂ heterostructure is contrary to expectations of simple van-der Waals stacked materials. The high quality of the samples will enable further studies of the spin state of the graphene and MoS₂ substrate as well as enable preparation of other heterostructure materials and thus will give a detailed description of the interaction in these heterostructure systems.

8:00pm **TF+NM-MoE8 Universality of Seebeck Coefficients in Graphene/h-BN Nano-Composites**, *Yosuke Ayako, A. Akaishi, J. Nakamura*, The University of Electro-Communications (UEC-Tokyo) and JST-CREST, Japan

Thermoelectric materials have attracted much attention because of their promising applications in power generation. Recently, we have shown that the superlattices consisting of zigzag graphene nanoribbons (GNRs) and BN nanoribbons (BNNRs) have giant Seebeck coefficients [1]. Such giant Seebeck coefficients of the superlattice models stem from the so-called pudding-mold band with a finite energy gap [2]. Although such types of superlattices have great fascination with thermoelectricity, the experimental synthesis of these two-dimensional structures may be an extremely-challenging task.

In the present study, we suggest more easy-to-make, practical one-dimensional structures possessing the pudding-mold band. We propose the graphene/h-BN hybrid nanoribbons with zigzag edges (hereafter referred to as “nano-composites”), in which both edges of GNRs are terminated with BNNRs. In this study, we specify the models using integer n and m , which are the numbers of dimer lines of GNRs and BNNRs, respectively. The Seebeck coefficients of nano-composites have been evaluated on the basis of the Boltzmann transport theory. Electronic band structures have been calculated using the first-principles calculations within the framework of the density functional theory. We have also employed the armchair nano-composites for comparison.

We have shown that the pudding-mold bands have been confirmed for the zigzag nano-composites, but not for the armchair ones. The Seebeck coefficients for the zigzag nano-composites decrease monotonically with increasing n . Their maximum values become higher than those for graphene and GNRs, though not to the extent of the superlattices [1]. On the other hand, the Seebeck coefficients for the armchair nano-composites do not become higher compared with those for the pristine armchair GNRs, since the mechanism of the enhancement based on the pudding-mold band does not work for these composites. Here, we should not overlook that the Seebeck coefficients for the armchair nano-composites show the oscillatory-decreasing behavior with increasing n , and their dependence on n can be classified into three categories of $3n$, $3n+1$, and $3n+2$, being analogous to the electronic structure of the zigzag carbon nanotubes [3]. Nevertheless, the Seebeck coefficients shows the universal dependence on the band gaps: the maximal, absolute Seebeck coefficient depends only on the bandgap irrespective of the structural category of nano-composites.

[1] Y. Yokomizo and J. Nakamura, *Appl. Phys. Lett.* **103**, 113901 (2013).

[2] K. Kuroki *et al.*, *J. Phys. Soc. Jpn.* **76**, 083707 (2007).

[3] R. Saito *et al.*, *Physical Properties of Carbon Nanotubes* (Imperial College Press, 1998).

8:20pm **TF+NM-MoE9 Reduction of Oxygen on Nitrogen-Doped Graphene**, *Akihito Ichikawa, A. Akaishi, J. Nakamura*, The University of Electro-Communications (UEC-Tokyo) and JST-CREST, Japan

Recently, several groups have reported high oxygen reduction reaction (ORR) activities in nitrogen-doped carbon nanomaterials which are candidates of metal-free catalysts for ORR [1]. Lee *et al.* have successfully fabricated nitrogen-doped graphene with the high ORR activity in acid media [2]. It has been confirmed that local atomic configurations of dopants in nitrogen-doped graphene are classified into three functional groups (pyrrole-like, pyridine-like, and graphite-like configurations) [3]. However, the mechanism of the ORR on the nitrogen-doped graphene has not fully understood.

In this work, we examine the ORR on the nitrogen-doped graphene containing the graphite-like N in a basal plane using first-principles calculations. In general, the ORR occurs mainly two pathways: The two-electron pathway ($2e^-$) that is reduced to hydrogen peroxide (H_2O_2), and the direct four-electron pathway ($4e^-$) that reduces to water (H_2O). Thermodynamic electrode potentials of each process at standard conditions are about 0.68V ($2e^-$) and 1.23V ($4e^-$), respectively. In case of the associative mechanism for the two- and four- electron reduction pathways, the electrocatalytic activity is governed by the stability of reaction intermediates like OOH^* , OH^* , and O^* (where “*” refers to a surface site). Free energies of the reaction intermediates have been calculated based on the computational hydrogen electrode model suggested by Norskov *et al.* [4]. We have taken account of effects of electrode potential, Φ of a solution, a local electric field in double layer, and water environment.

We have constructed energy diagrams at several electrode potentials on the basis of the first-principles calculations. It has been shown that the $2e^-$ and $4e^-$ reduction processes proceed at potentials up to about 0.5V and 0.8V, respectively. This means that we can control the reduction pathway for the nitrogen-doped graphene with the graphite-like N. Proton-electron transfer to OOH^* (the $2e^-$ pathway), and the formation of OOH^* (the $4e^-$ pathway) are confirmed to be the rate-limiting steps, respectively. The effects of electric field and water environment will also be discussed in the presentation.

Reference:

[1] J. Ozaki, N. Kimura, T. Anahara, A. Oya, *Carbon* **45**, 1847 (2007).

[2] K. R. Lee, K. U. Lee, J. W. Lee *et al.*, *Electrochem. Commun.* **12**, 1052 (2010).

[3] H. Niwa, K. Horiba, M. Oshima *et al.*, *J. Power Sources* **187**, 93 (2009).

[4] J. K. Norskov, J. Rossmeisl, A. Logadottir, L. Lindqvist, *J. Phys. Chem. B* **108**, 17886 (2004).

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