

Thin Films

Room: Makai - Session TF-ThM

Graphene

Moderator: Suneel Kodambaka, University of California, Los Angeles

8:00am **TF-ThM1 Construction and Characterization of Two Dimensional Atomic Crystals on Transition Metal Surfaces: Graphene, Silicene, Germanene, and Hafnene, Shixuan Du**, Institute of Physics, Chinese Academy of Sciences, China **INVITED**

Epitaxy on a transition metal (TM) substrate is a promising method to produce a variety of two dimensional (2D) atomic crystals which potentially can be used in next generation electronic devices. This method is particularly valuable in the case of producing 2D materials that do not exist in 3D forms, for instance, silicene. In this talk, I will present construction and characterization of graphene, silicene, germanene, and hafnium honeycomb lattice on transition metal surfaces (TMS) (for example, Ru(0001), Pt(111), and Ir(111)). Molecular beam epitaxial growth technique is used to form the large scale 2D atomic crystals on TMS. Low electron energy diffraction (LEED) and scanning tunneling microscopy/spectroscopy (STM/S) together with density functional theory (DFT) calculations are employed to confirm the formed structure on the TMS. We expect that on the TMS more new 2D crystals could be found and these materials will show very interesting physical property and its promising potential applications in nanoscale devices.

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8:40am **TF-ThM3 Graphitic Structures on Ru(0001), Valeria del Campo**, Universidad Tecnica Federico Santa María, Chile, *R.H. Henríquez*, Universidad Técnica Federico Santa María, Chile, *P.H. Häberle*, Universidad Tecnica Federico Santa María, Chile

Chemical Vapor Deposition (CVD) is one of the most used techniques for growth of graphitic structures. In the case of graphene, this technique allows the growth of large graphene sheets. However, to obtain monocrystalline graphene (millimeter scale) the CVD process is performed in Ultra High Vacuum (UHV). In this work we grew monocrystalline graphene and carbon nanodiscs on Ru(0001) through LP-CVD (Low Pressure CVD).

To grow our samples, first we heat the substrate (ruthenium crystal) in UHV. Once the desired temperature has been reached, the substrate is exposed to ethylene for some minutes. After exposure, the sample is annealed to allow the formation of carbon structures on the substrate. We performed this process with two different sets of parameters, obtaining different carbon structures on the Ru(0001) surface.

With one set of parameters we obtained graphene sheets on the ruthenium surface. With the second set of parameters we also grew a graphene layer, but on top of this layer we grew carbon nanodiscs. The diameters of these discs vary from few to hundreds nanometers, while their height is always below 1 nm.

The growth of carbon nanodiscs could be explained not only by the different set of parameters but also by the presence of impurities on the ruthenium surface. These impurities enable a preferential nucleation around them. This carbon excess allows the formation of carbon nanodiscs under the CVD conditions used in this experiment.

9:20am **TF-ThM5 On the Wettability of Graphene, Akira Akaishi**, The University of Electro-Communications (UEC-Tokyo) and JST-CREST, Japan, *T. Yonemaru*, The University of Electro-Communications (UEC-Tokyo) and JST-CREST, *J. Nakamura*, The University of Electro-Communications (UEC-Tokyo), Tokyo, Japan

While graphite is well known as hydrophobic material, recent studies have revealed that pristine graphitic surfaces are more likely to be hydrophilic. Hydrophobic/hydrophilic nature is closely related to wettability of surfaces. One of the characteristic measures of wettability is a contact angle that is the angle of the edges of a water droplet placed on target surfaces. It has been reported that the contact angle of water on graphite surfaces decreases as removing hydrocarbons on the surface [1,2]. The contact angle estimated

by molecular dynamics (MD) simulations, however, varies depending on a choice of the parameters of interaction potentials between a water molecule and graphitic surfaces [3]. The wettability of pristine graphene surfaces remains unsettled.

We have investigated the behavior of water molecules on graphene surfaces with MD simulations by changing empirical parameters. The simulations are prepared with a graphene sheet and a water droplet which is dropped initially on the graphene surface. With increasing the number of water molecules, the droplet covers the surface and the layered-structure of molecules on the surface is formed. This indicates that, at a level of empirical model, a graphene surface is capable of wetting.

The formation of water layers on the surface can be seen by the density profile of water molecules. The density distribution of oxygen and hydrogen atoms of water along the axis perpendicular to the graphene surface indicates the existence of the layers. Moreover, the distinct peaks of the hydrogen atom distributions indicate that the direction of oxygen-hydrogen (O-H) bonds is not randomly distributed but is certainly oriented. The angle distribution of O-H bonds shows that hydrogen bonds are formed between the water layers on the graphene surface. In other words, the water molecules in the layers tend to form the hydrogen bonding only within the layers. The water molecules above the layer have no unpaired hydrogen bonds that are pointing perpendicular to the layer plane.

References

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- [2] A. Kozbial *et al.*, *Carbon* **74**, 218 (2014)
- [3] T. Werder *et al.*, *J.Chem.Phys.B* **107**, 1345 (2003)

9:40am **TF-ThM6 Unbalanced Standing Wave Patterns at a Graphene Junction, W.-J. Jang, H. Kim**, Korea University, Seoul, Republic of Korea, *M. Wang, S.K. Jang*, Sungkyunkwan University (SKKU), Republic of Korea, *M. Kim*, SKKU Advanced Institute of Nanotechnology (SAINT), Sungkyunkwan University (SKKU), Suwon 440-746, Republic of Korea, *S. Lee, S.-W. Kim, Y.-J. Song*, Sungkyunkwan University (SKKU), Republic of Korea, *Se-Jong Kahng*, Korea University, Republic of Korea

Exotic behaviors such as lensing and perfect transmission are expected in graphene p-n junctions, due to lattice-induced chirality of charge carriers, and experimentally studied using charge transport devices with a scale of several tens of nanometers. However, there has not been a study to confirm such behaviors at the atomic scale. Here, we report the experimental evidence for chiral electron reflections at a graphene junction on hexagonal BN/Cu. We performed scanning tunneling microscopy and spectroscopy to observe unbalanced electron standing wave patterns, which only appeared in one region at an energy lower than 100 meV, or at higher than 250 meV in the other region. Such an energy-dependent crossover of regions of standing wave patterns is explained by solving the Dirac equation with a simple potential step model. Our study shows that chirality of the charge carrier is a key component for understanding their reflections in graphene junctions at the atomic scale.

11:00am **TF-ThM10 Synthesis of Graphene via Surface Segregation and Reaction, Daisuke Fujita**, NIMS, Japan, *K. Sagisaka, H. Guo*, National Institute for Materials Science, Japan

Single-layer, bi-layer and few-layer thick nanosheets of graphene have been attracting significant amount of attention due to their excellent physical, chemical and mechanical properties. The first isolation of few-layer graphene (FLG) was demonstrated in 2004. However, single-layer graphene (SLG) was first synthesized 40 year ago by *surface segregation*, and was identified by Blakely *et al.* in 1974 using surface sensitive techniques. In 1980s, we initiated the growth and characterization of FLG and h-BN nanosheets using surface segregation and *surface reaction*. For the graphene growth, there are three important steps; surface segregation of doped atoms, surface reaction to form a monolayer phase, and subsequent 3-D growth (*surface precipitation*). Such surface phase transition was demonstrated on C-doped Ni(111) by *in situ* X-ray photoelectron spectroscopy (XPS) at elevated temperatures, and the growth mode was clarified by inelastic background analysis. Among the three, the surface segregation plays the most important role for the SLG synthesis. The surface segregation approach has been applied to Pt(111) and Pd(111) substrates, where weak coupling is expected, and controllable growth has been demonstrated successfully. As one of the derivatives, we recently proposed a promising method for producing SLG covering an entire substrate at low temperature using a Ni film deposited on an HOPG substrate. By heating the Ni/HOPG in high vacuum, carbon atoms forming graphene are diffused from the HOPG substrate through the Ni template. In this paper, we will put more focus on the effect of competitive surface-site occupation between carbon

and other surface-active impurities on the SLG growth. It is known that sulfur is a typical impurity of metals and the most surface-active element. Even with a high purity single crystal, the surface sites are finally occupied by sulfur at the elevated temperatures by surface segregation. In the case of Ni(110) surface, it is confirmed by scanning Auger microscopy (SAM) and scanning tunneling microscopy (STM) that the available surface sites is nearly occupied by sulfur with a centered 2x2 arrangement. When the Ni(110) is doped with carbon, surface segregation of carbon and following graphene growth shall be strongly affected or restricted by the surface active elements such as sulfur. In this situation, we discovered a strongly directional growth of SLG, exhibiting rectangular-like shapes and nearly straight step edges. The detailed characterization at the nanoscale and interesting growth mechanism shall be discussed based on high resolution microscopes like UHV-STM and scanning helium ion microscopy (SHIM).

11:20am **TF-ThM11 Anomalous Enhancement of Seebeck Coefficients for the Graphene/h-BN Superlattices**, *Jun Nakamura*, The University of Electro-Communications (UEC-Tokyo), Tokyo, Japan, *Y. Yokomizo*, The University of Electro-Communications (UEC-Tokyo) and JST-CREST

The thermoelectric conversion has been of interest for many researchers since Hicks and Dresselhaus showed that the introduction of low-dimensional structures such as quantum well structures would significantly enhance the dimensionless figure of merit [1]. Graphene is a two-dimensional, mono-layer material having honeycomb lattice of carbon atoms [2,3]. It has been suggested that the graphene-based device can be a novel thermoelectric material because of its potential giant Seebeck coefficient larger than 30 mV/K [4]. On the other hand, graphene nanoribbon (GNR) is a one-dimensional (1D) material, a strip of graphene, which has also been investigated theoretically as thermoelectric materials. A molecular dynamics study has shown that a high figure of merit can be obtained for the zigzag GNR (ZGNR) [5]. This result implies that the introduction of 1D structural modulation makes graphene into novel thermoelectric materials. We hereby propose, in this study, superlattice models consisting of ZGNR and zigzag BN nanoribbon (ZBNRR) [6,7]. We have investigated the Seebeck coefficients of ZGNR/BNNRs within the Boltzmann transport theory. It has been shown that a ZGNR/ZBNRR marks up to 20 times larger in the Seebeck coefficient than graphene. The Seebeck coefficients of the superlattices increase with decreasing width of the constituent ZGNR. It has been revealed that the giant Seebeck coefficients of the superlattices stem from the so-called pudding mold band with a finite energy gap.

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11:40am **TF-ThM12 All-graphene Gas Sensor Integrated with Sensing Channel and Graphene Heater**, *Choon-Gi Choi*, Creative Research Center for Graphene Electronics, Electronics and Telecommunications Research Institute (ETRI), Republic of Korea

Graphene leading to high surface-to-volume ratio and outstanding conductivity has been applied for gas molecule sensing with fully utilizing its unique transparent and flexible functionalities which cannot be expected from solid-state gas sensors. However, in order to realize the fast responsive and significantly sensitive graphene gas sensor without hampering of both flexibility and transparency, the high quality of sp² carbon bonding for sharp sensing response are demanded. In this work, we demonstrate large-scale flexible and transparent gas molecule sensor devices, integrated with a graphene sensing channel and a graphene transparent heater for fast recovering operation. This combined all-graphene device structure enable an overall device optical transmittance that exceeds 90% and reliable sensing performance with a bending strain of less than 1.4 %. In particular, we could classify the fast (~14 s) and slow (~95 s) response due to sp²-carbon bonding and disorders on graphene and the self-integrated graphene heater leads to the rapid recovery (~11 s) of a 2 × 2 cm² sized sensor with reproducible sensing cycles, including full recovery steps without significant signal degradation under exposure to NO₂ gas.

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