

Thin Films

Room: Makai - Session TF-MoM

Self-Organized and Nanostructured Thin Films

Moderator: Shixuan Du, Institute of Physics, Chinese Academy of Sciences

8:40am **TF-MoM1 Growth Kinetics, Structure, and Properties of 2D Layered Materials**, *Suneel Kodambaka*, University of California, Los Angeles **INVITED**

Two-dimensional (2D) layered materials owing to a wide range of properties (e.g., graphene is metallic, h-BN is insulating, and MoS₂ is semiconducting) have attracted immense attention over the past decade for a variety of optoelectronic and nanoelectronic applications. Recent efforts have focused on vertical integration of 2D layers of dissimilar materials (e.g., graphene/h-BN and graphene/MoS₂). In these heterostructures, due to relatively weak van der Waals interactions, orientational registry between the layers is not expected and is often difficult to control. This talk will focus on the effect of interlayer orientation on the electronic structure of the resulting heterostructures. Using a combination of *in situ* low-energy electron microscopy (LEEM) and density functional theory (DFT) calculations, we investigated the electronic properties of graphene/Pd(111). From the LEEM images we determined the graphene growth kinetics and measured graphene work function as a function of orientation and layer thickness. Recently, we extended our DFT calculations to study the electronic structures of h-BN/Ni(111) and graphene/MoS₂ heterostructured layers. We found that hBN can chemisorb or physisorb on Ni(111), with metallic or insulating properties, respectively and these properties are not altered when graphene is placed atop hBN. For graphene on MoS₂, we found that rotating graphene layer by 30° with respect to MoS₂ changes the MoS₂ band gap from 1.68 eV direct to 1.56 eV indirect. We attribute the observed orientation-dependent bandgap to the variation in the S-S interplanar distance with the MoS₂-graphene interlayer orientation.

9:20am **TF-MoM3 Deposition and Tribomechanical Properties of Hf-B-C Thin Films**, *Elham Mohimi, T. Ozkan, S. Babar, P.J. Sempstrott*, University of Illinois at Urbana-Champaign, USA, *A.A. Polycarpou*, Texas A&M University, *G.S. Girolami, J.R. Abelson*, University of Illinois at Urbana-Champaign, USA

The tribomechanical properties of thin film coatings can be enhanced by alloying to afford a multicomponent nanostructure. Our group previously reported the conformal growth and favorable mechanical properties of HfB₂ and Hf-B-N hard coatings by chemical vapor deposition (CVD) at low substrate temperature. Here, we alloy C into HfB₂ in order to reduce the friction coefficient and enhance the hardness. A useful analogue is C-alloyed TiB₂, which exhibits super hardness and good thermal stability. However, there have been no previous studies of Hf-B-C alloys.

Hf-B-C nanocomposite coatings are deposited by CVD onto Si or stainless steel discs using the precursor hafnium borohydride, Hf(BH₄)₄, with a co-flow of dimethylbutene (DMB), (CH₃)₃CCCH=CH₂, as the carbon source. Depositions are performed in a high vacuum chamber with base pressure of 10⁻⁸ Torr, hafnium borohydride pressure 0.1-0.5 mTorr and DMB pressure 0.05-0.4 mTorr at substrate temperatures of 250-600°C. DMB also acts as growth inhibitor – it reduces the film growth rate by a factor of 2-6 compared to growth using the precursor alone, an effect which enhances conformality. For higher temperature growth, DMB increases the film density and decreases the surface roughness. XPS analysis indicates a mixture of HfB₂, HfCx and B4C phases, however, this is uncertain due to the small shifts between different bonding states.

As-deposited films are XRD amorphous with hardness values of 9-26 Gpa and reduced modulus of 99-208 Gpa. Upon annealing at 700°C for 3 hours under inert gas atmosphere, the films transform to a partially nanocrystalline structure, which increases the hardness to 17-34 Gpa and the elastic modulus to 158-248 Gpa. The tribological properties of Hf-B-C films are superior to those of HfB₂ films. This is attributed to graphitic attachment of carbon atoms on contacting surfaces as evidenced by EDS analysis of the wear scar surface. Summarizing, this system affords conformal growth at low growth temperatures, suitable for the fabrication of complex structures such as MEMS.

9:40am **TF-MoM4 Effect of Chemical Reaction on Low Friction of Diamond-Like Carbon in Water Lubrication : A Theoretical Study**, *Shandan Bai, Y. Niiyama, Y. Kobayashi, Y. Higuchi, N. Ozawa, K. Adachi, S. Mori, K. Kurihara, M. Kubo*, Tohoku University, Japan

[Introduction] Diamond-Like Carbon (DLC) coatings have low friction and anti-wear tribological performances. Furthermore, water lubrication improves the friction properties of DLC films and reduces the emission of CO₂. The friction coefficient of the DLC films drastically changes under water lubrication, since some tribo-chemical reactions occur during the sliding. However, tribo-chemical reactions are difficult to be revealed only by experimental analyses in details. The computational technique is efficient method to investigate the low friction mechanism [1]. In this study, we reveal the tribo-chemical reaction between DLC film and water using the computational method on an atomic scale.

[Method] To clarify the tribo-chemical reactions of DLC films under water lubrication, we use our tight-binding quantum chemical molecular dynamics (TB-QCMD) method [2]. We construct the sliding simulation model consisting of 80 water molecules and two DLC substrates. The thickness of water is approximately 1.0 nm. The friction simulation is performed for 100,000 steps with the time step of 0.1 fs. We apply contact pressures of 0.5 and 5 GPa on the top layer of upper substrate of DLC films, while it is forcibly slid with a horizontal velocity of 10 m/s. The simulation temperature is set at 300 K, achieved by velocity scaling method.

[Results and Discussion] We perform our TB-QCMD calculations to investigate the low friction properties of DLC in water lubrication. Under a contact pressure of 0.5 GPa, one C-OH bond is generated on the DLC surface at 0.045 ps during the sliding, because of the dissociation of a water molecule. Furthermore, at 3.655 ps, we observe another C-OH bond generation on the surface. The result indicates that OH terminates the DLC surface under a contact pressure of 0.5 GPa. Under a contact pressure of 5 GPa, generation of a C-OH bond is observed on the surface at 1.380 ps. Furthermore, at 3.880 ps, it is very interesting to see the generation of C-O-C on the DLC surface, which is a different chemical reaction with that under pressure of 0.5 GPa. The friction coefficients are 0.81 and 0.05 under contact pressures of 0.5 and 5 GPa, respectively. Those results indicate that the friction coefficient decreases with increasing a contact pressure. We think that the chemical reaction leads to the structure change on the DLC surface and the low friction properties of DLC in water lubrication under high contact pressures.

[1] S. Bai, M. Kubo et al., J. Phys. Chem. C, 116, 12559, (2012).

[2] S. Bai, M. Kubo et al., RSC Adv., DIO: 10.1039/c4ra04065a.

10:20am **TF-MoM6 Growth of Large-Area 2D Transition Metal Dichalcogenides**, *Lain-Jong Li*, King Abdullah University of Science and Technology, Saudi Arabia **INVITED**

The direct-gap property of the semiconducting transition metal dichalcogenide (TMD) monolayers is attractive for optoelectronics and energy harvesting. Here I would like to discuss the synthetic approaches to obtain crystalline and sub-mm sized MoS₂, WSe₂ and WS₂ monolayers directly on arbitrary substrates using vapor phase reaction between metal oxides and S or Se powders.^{1,2} These layer materials can be transferred to desired substrates, making them suitable building blocks for constructing multilayer stacking structures. By using micro-beam X-ray photoelectron spectroscopy, we report the determination of band offsets in TMD heterostructures.³ These physical quantities are fundamentally important for novel devices based on heterostructures formed between dissimilar TMDs. Some possible applications based on TMD heterostructures will be discussed.

References

¹ Huang, J. K. et al. Large-Area Synthesis of Highly Crystalline WSe₂ Monolayers and Device Applications. *Acs Nano* 8, 923 (2014).

² Lee, Y. H. et al. Synthesis of Large-Area MoS₂ Atomic Layers with Chemical Vapor Deposition. *Advanced Materials* 24, 2320 (2012).

³ M.-H. Chiu et al. Determination of band alignment in transition metal dichalcogenides heterojunctions. arXiv:1406.5137

11:00am **TF-MoM8 Influence of Testing Conditions on the Tribological Behaviour of C(N)-WS₂ Self Lubricating Thin Films**, *Albano Cavaleiro, M. Evaristo*, University of Coimbra, Portugal, *T. Polcar*, University of Southampton, UK

Transition metal dichalcogenides (TMD) have a layered structure and weak inter-layer bonding allowing to display very low friction coefficient when a tangential force is applied. Being sliding contact a surface phenomenon, these materials have been largely studied in the form of thin coatings.

Whenever conditions exist for establishing stronger bonds between the layers, the friction coefficient can significantly increase. This is the reason why the industrial applicability of these coatings is still very limited due to the deficient tribological behavior in humid atmospheres, for which strong bonds can be formed through oxygen. In order to overcome this problem different approaches were followed based on alloying TMD with different elements. Among these elements, our group has developed a deep study on the addition of carbon and nitrogen. We have proved, as it was already known, that the friction coefficient could increase from the range [0.005 – 0.05] up to [0.05 – 0.3] when the coatings were tested in dry or in humid conditions, respectively.

The aim of this talk is to present a systematic study concerning the influence of humidity in the tribological behavior of TMD+C coatings. We deposited W-S-C coatings with increasing C content up to 60 at.% with two S/W ratios, close to 1.4 and 1.0. These coatings were tested by pin-on-disk in different humidity range from RH=20% up to RH=95%. Contrarily to what we have observed in previous studies, we could not find any case where the friction coefficient went down lower than 0.1. Furthermore, there was no clear trend on the effect of either the humidity or the S/W ratio on the friction coefficient. The detailed analysis of the sliding surfaces allowed to conclude that, in all tests, orientation of WS₂ crystals in the top sliding contact could not be achieved. The comparison with previous deposited W-S-C coatings allowed to conclude that the different tribological behavior could be attributed to a different nanostructure arrangement in the as-deposited conditions.

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