

## Surface Science Division Room 25 - Session SS-WeM

### Deposition and Growth at Surfaces

**Moderators:** Kathryn Perrine, Michigan Technological University, Arthur Utz, Tufts University

8:00am **SS-WeM-1 Metal Growth on and under Graphene: Morphology, Intercalation and Magnetization, Michael Tringides**, Iowa State University and Ames Laboratory

**INVITED**

Graphene based electronic and spintronic devices require understanding the growth of metals on graphene. Several metals (Gd, Dy, Eu, Fe, Pb) deposited on epitaxial graphene were studied with STM, SPA-LEED and DFT. For practically all metals the growth mode is 3-d[1,2]. This is a result of the low ratio of the metal adsorption to metal cohesive energy and repulsive interactions between unscreened charges at the metal-graphene interface that favor islands of small "footprint". It is an open challenge to find ways to modify the growth to layer-by-layer for high quality metal contacts and graphene applications as a spin filter. By growing Dy at low temperatures or high flux rates it is found that upward adatom transfer is kinetically suppressed and layer-by-layer is possible[3]. These results are also relevant for metal growth on other 2-d van der Waals materials that also have weak bonding with metals and favor 3-d metal growth. Some of the grown metals are also characterized magnetically. Ex situ SMOKE magnetization measurements on the grown Fe islands show a transition from superparamagnetic to ferromagnetic islands with coverage. XMCD measurements on Dy islands which grow with fcc(111) crystal structure (instead of the bulk hcp Dy structure) show that the islands are paramagnetic.

The graphene-metal interaction is also important for metal intercalation which provides a novel way to tune graphene's properties, besides doping. However many issues related to the intercalation process itself are poorly understood, i.e., the temperature and entry points where atoms move below graphene, different intercalation phases, their coverage, etc. SPA-LEED and STM were used to study these questions for Dy intercalation. Spot profiles of several spots (specular,  $6sq(3)$ , graphene) are studied as function of temperature and electron energy to deduce the kinetics of intercalation and the layer where the intercalated atoms reside.

Dy nucleation experiments were performed on graphene partially intercalated with Dy. The results show that nucleation is preferred on the intercalated than on the pristine areas. Difference in doping between the two areas generates an electric field that transforms random walk to directional diffusion and accounts for the guided nucleation[4]. This can be a general method to control patterning of metallic films on graphene.

In collaboration with M. Hupalo, P. A. Thiel, M T Hershberger, D. McDougall, C.Z. Wang.

#### References

1. M. Hupalo et al *Advanc. Mater.* 23 2082 (2011) 2. X. Liu, et al. *Progr. Surf. Sci.* 90 397 (2015) 3. D. Mc Dougall et al *Carbon* 108 283 (2016) 4. X. Liu et al. *Nano Research* 9(5): 1434 (2016)

8:40am **SS-WeM-3 Nonequilibrium Growth of an Ordered ZnTPP Overlayer on a Ag(100), Robert Bartynski**, Rutgers, the State University of New Jersey; P Kim, S Rangan, Rutgers University; C Ruggieri, Rutgers, the State University of New Jersey; D Lu, CFN, Brookhaven National Laboratory; S Whitelam, The Molecular Foundry, LBNL

Although there have been many studies characterizing the self-assembling process of organic molecules at metal surfaces, how the competition between substrate-molecule interactions and intermolecular forces impacts molecular arrangement during overlayer growth remains poorly understood. To address this question we have investigated the adsorption kinetics that leads to self-assembly of a non-equilibrium phase of zinc(II) tetraphenylporphyrins (ZnTPP) upon direct deposition on the Ag(100) surface in ultra-high vacuum (UHV).

When deposited directly onto the Ag(100) surface, the overlayer assumes a highly ordered "2+1" adsorption geometry consisting of two rows of molecules with identical registry with the surface atoms adjacent to a third row of molecules that are translated and rotated with respect to the other two rows. This structure reorganizes to the thermodynamically stable (1+1) phase upon annealing, indicating that the 2+1 geometry is a kinetically trapped growth phase.

Scanning tunneling microscopy was used to determine registry and symmetry of as-deposited and annealed ZnTPP monolayers grown in-situ on the Ag(100) surface under UHV conditions. Density functional theory (DFT) has been utilized to calculate the electronic structure and energetics of the systems, while kinetic Monte Carlo (KMC) simulations were used to model the self-assembly process. These calculations suggest that, while intermolecular interactions are primarily responsible for the thermodynamically-preferred phase, owing to the reduced number of nearest neighbors at the grow front, molecule-substrate interactions gain importance leading to the metastable 2+1 striped phase. Recent evidence pointing to the role of surface stress and molecular conformation in determining the geometry of ZnTPP on the Au(111) surface suggests that these considerations may also give rise to the non-equilibrium (2+1) phase of ZnTPP/Ag(100) [1]. This study gives insight into the fundamental mechanisms behind the self-assembly process that is not observed under multilayer deposition.

[1] Ruggieri, C., et al. Zinc (II) Tetraphenylporphyrin on Ag (100) and Ag (111): Multilayer Desorption and Dehydrogenation. *J. Phys. Chem. C.* **2016**, *120*, 7575-7585.

9:00am **SS-WeM-4 Growth and Motion of Liquid Alloy Droplets of Au on Ge(110), B Stenger, A Dorsett, J Miller, E Russell, C Gabris, Shirley Chiang**, University of California Davis

The growth of Au on Ge(110) was observed with low energy electron microscopy (LEEM). The objectives of this study were to control the growth of low-dimensional nanostructures and understand the temperature induced motion of islands. Ge(110) was dosed with 0.5-5 ML of Au and heated to 850°C. During deposition, liquid eutectic alloy islands formed on the surface and grew to ~1-2  $\mu\text{m}$  in width and ~2-5  $\mu\text{m}$  in length, elongated along the [1,-1,0] direction due to an anisotropy in the dissolution rate of the substrate. Low energy electron diffraction (LEED) showed a transition from a (4x5) phase to a (2x1) phase immediately preceding island growth. A temperature gradient of 0.017°C/ $\mu\text{m}$  across the surface induced a Ge concentration gradient in the islands and diffusion of Ge through the islands from high to low temperature. Dissolution of Ge at the undersaturated high temperature end of the island and crystallization of Ge at the supersaturated low temperature end resulted in movement of the islands toward higher temperature. Smaller islands, unable to overcome pinning effects, remained stationary, while larger islands moved with velocities of 0.1-1.0  $\mu\text{m/s}$ . Island velocities are consistent with a model of diffusion limited motion. Upon collision islands merged, increasing in size up to ~60  $\mu\text{m}$  in width and ~100  $\mu\text{m}$  in length. The direction of movement was restricted to the [1,-1,0] direction by the same dissolution anisotropy that causes island elongation during the growth process, with the exception of very large islands for which the direction was determined only by the temperature gradient. Optical microscopy confirmed that the largest islands moved from the cooler edges of the sample toward the hotter center of the sample. As the temperature decreased, the island behavior was also studied and revealed rapid island contractions as Ge crystallizes out from the islands, leaving a visible outline of the original extent of the island.

9:20am **SS-WeM-5 Photodeposition of Pt Clusters on HOPG Supported TiO<sub>2</sub> Nanoparticles: Development of a Nanomaterial Model Catalyst System, Jared Bruce, A Babore, R Galhenage, J Hemminger**, University of California Irvine

Model heterogeneous catalysts are traditionally studied using well-defined single crystal surfaces. However, industrial applications of these catalysts do not involve well-defined crystal surfaces but are comprised of colloids and other small crystallites. Development of a more representative model system, where nanomaterials and colloids of the active catalyst material are supported on an oxide nanoparticle, will enable rigorous investigation under relevant catalytic conditions.

TiO<sub>2</sub> is a stable oxide material that can be used to support an active catalyst material such as platinum. Our group has shown that physical vapor deposition can be used to create TiO<sub>2</sub> nanoparticles supported on highly oriented pyrolytic graphite (HOPG). TiO<sub>2</sub> nanoparticles are ideal for photodeposition of platinum using low concentrations of a chloroplatinate salt in aqueous conditions to control the amount of Pt deposited on the surface. Initially, the Pt deposits as a Pt (IV) oxide material as observed by X-ray photoelectron spectroscopy (XPS) and can be reduced to Pt (II) species by continued irradiation in the absence of the chloroplatinate salt in solution. Interestingly, we have not observed a complete conversion to Pt (0) and only upon heating to 400K in vacuum do we observe the presence of the Pt (0) species. We have also used temperature

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programmed desorption (TPD) to characterize the change in water desorption thermodynamics when Pt has been deposited on the surface of the TiO<sub>2</sub> nanoparticles. When Pt is present on the surface, there is a shift to lower temperatures in the monolayer and second layer desorption states. The relative shift is dependent on the total amount of Pt present on the surface of the TiO<sub>2</sub>.

9:40am **SS-WeM-6 In Vacuo Low-energy Ions Scattering Studies of ZrO<sub>2</sub> Growth by Magnetron Sputtering**, *Marko Sturm, R Coloma Ribera, R van de Kruijs, A Yakshin, F Bijkerk*, MESA+ Institute for Nanotechnology, University of Twente, Netherlands

ZrO<sub>2</sub> thin films have applications as dielectric or passivation layer in applications as CMOS gate dielectrics and Si solar cells. Furthermore, ZrO<sub>2</sub> may be of interest as capping layer for protecting extreme ultraviolet (EUV) optics against chemical degradation processes. For these applications, it is critical that a homogeneous closed film is formed, which does not degrade the underneath layers, while the thickness is, depending on application, often restricted to a few nanometres. In this work, we studied the initial growth of ZrO<sub>2</sub> films by reactive magnetron sputtering on top of amorphous Si (a-Si), SiN<sub>x</sub> and SiO<sub>2</sub> by *in vacuo* low-energy ion scattering (LEIS). Since LEIS is selectively sensitive for the outermost atomic layer, it could be determined for which deposited thickness a closed layer was formed and how deposition parameters and surface passivation affect the sharpness of the ZrO<sub>2</sub>/Si interface. The information from surface peaks of Zr, O and the a-Si substrate was compared with the so-called tail signal from particles that scatter on sub-surface Zr atoms. As example, we studied representative conditions for metallic and oxidic mode reactive magnetron sputtering. In oxidic mode, where more high energy particles are present in the deposition plasma, 3.4 nm of ZrO<sub>2</sub> was required to form a closed layer of ZrO<sub>2</sub> on Si. In metallic mode, with a lower O to Ar ratio, intermixing could be reduced by a factor 2, such that a closed film of ZrO<sub>2</sub> was formed at 1.7 nm deposited film thickness [1]. *In-vacuo* X-ray photoelectron spectroscopy (XPS) confirmed that the formation of Zr silicate at the ZrO<sub>2</sub>/Si interface was reduced in the case of metallic mode deposition. Passivation of Si by reactive deposition of a SiN<sub>x</sub> or SiO<sub>2</sub> barrier layer between the ZrO<sub>2</sub> and Si did not change the required ZrO<sub>2</sub> thickness for forming a closed layer, most likely because the Zr silicate formed during deposition already passivates the Si substrate. Thermal annealing studies in ambient atmosphere showed that 2 nm ZrO<sub>2</sub> layers deposited with metallic mode sputtering protects the underlying a-Si substrate against oxidation up to 400 °C.

[1] R. Coloma Ribera, R.W.E. v.d. Kruijs, J.M. Sturm, A.E. Yakshin and F. Bijkerk, *J. Appl. Phys.* **121**, 115303 (2017)

11:00am **SS-WeM-10 Dihydrotetraazapentcene Growth on Alumina Thin Films and Sapphire: from the Submonolayer to nm Thick Films**, *Anthony Thomas, T Léoni, A Ranguis, L Masson, O Siri*, Aix-Marseille University, France; *B Kaufmann, A Matkovic, M Kratzer, C Teichert*, Montanuniversität Leoben, Austria; *C Becker*, Aix-Marseille University, France

Recently azaacenes have received increasing attention because of their semiconducting properties and their improved environmental stability as compared to acenes. Functionalizing acenes with N and NH groups may largely enhance intermolecular interactions and lead to a better order in nm-scale thin films. The interactions in those films are mediated either by H-bonding[1] or by dipole-dipole forces. In this context, the growth of Dihydrotetraazapentcene (DHTAP) on alumina surfaces has been studied using scanning tunneling microscopy (STM) and atomic force microscopy (AFM) at different temperatures (from 220 K to 360 K and 280 K to 390 K, respectively). For the STM measurements, DHTAP was deposited by molecular beam epitaxy in a coverage range from 0.4ML to 3.6ML on an ultra-thin Al<sub>2</sub>O<sub>3</sub> film on Ni<sub>3</sub>Al(111) [2]. For the AFM investigations, DHTAP (coverage range 0.4 nm to 1.7 nm) was deposited by hot-wall epitaxy on sapphire(0001) single crystal surfaces. Both, the STM and the AFM measurements show a strong dependence of the growth mode on temperature. Indeed, higher temperatures lead to fewer but bigger islands when the flux is kept constant in accordance with the common model of heterogeneous nucleation. The STM results clearly indicate a dewetting of DHTAP on the surface. It could also be shown that the emerging islands are well ordered. Two structures can be observed where the molecules are standing-up on the surface with a slight angle between their long axis and the surface normal, probably due to the steric hindering. The AFM results revealed that terraced islands and curved needle-like structures emerge above 330 K. Moreover, the islands observed by STM have step heights corresponding to upright standing molecules. Finally, the length and curvature of the needle-like structures show a clear dependence on the temperature, they are longer and more curved for higher temperatures.

We try to understand how the crystalline structure of nm-sized islands overserved by STM influences the island morphology observed for thicker films by AFM.

[1] T. Lelaidier, T. Leoni, P. Arumugam, A. Ranguis, C. Becker, O. Siri, *Langmuir* **30**, 5700-5704 (2014)

[2] S. Degen, A. Krupski, M. Kralj, A. Langner, C. Becker, M. Sokolowski, K. Wandelt, *Surf. Sci.* **576**, L57 – L64 (2005)

11:20am **SS-WeM-11 Zintl Template Formation and Function during Atomic Layer Deposition Growth of Crystalline Perovskites on Ge (001)**, *Shen Hu, A Posadas, A Demkov, J Ekerdt*, The University of Texas at Austin

The growth SrTiO<sub>3</sub>, SrZrO<sub>3</sub> and BaTiO<sub>3</sub> perovskites on Ge (001) has been achieved by atomic layer deposition (ALD). We find that the initial dosing of the barium- or strontium-bis(triisopropylcyclopentadienyl) precursors on a clean Ge (001) surface forms the same Zintl template as 0.5-monolayer (ML) of Ba on Ge (001) when deposited by molecular beam epitaxy (MBE).<sup>1</sup> The procedure to produce a Zintl template is shown in Figure 1. The Zintl templates formed by both ALD and MBE display the same X-ray photoelectron binding energy shifts for Ba 3d, Sr 3d and Ge 3d and both surfaces result in symmetric Ge surface dimers. The surface core level shifts indicate charge transfer from the alkaline earth metal to the Ge surface. *In-situ* reflective high energy electron diffraction images demonstrate the same 2x1-reconstructed surface after using both molecular and atomic Ba sources. High-angle annular-dark-field scanning transmission electron microscopy further confirms all ALD-grown BaTiO<sub>3</sub>, SrZrO<sub>3</sub>, SrHfO<sub>3</sub> and SrHf<sub>0.55</sub>Ti<sub>0.45</sub>O<sub>3</sub> on Ge have the similar Zintl template interface structure as MBE-grown BaTiO<sub>3</sub> on Ge. Carbon, likely in the form of dissociated ligands, binds to the Ge (001) surface during precursor dosing and some of this carbon contaminates the interface after growth.

Herein we report the role of a Zintl template formed from 0.5-ML of elemental Ba in minimizing surface carbon contamination and facilitating crystal growth. SrZrO<sub>3</sub> films are grown using ALD on the templated-surface at 225 °C using strontium-bis(triisopropylcyclopentadienyl), tetrakis(dimethylamido) zirconium (IV) and H<sub>2</sub>O. The ALD chamber surfaces cannot be purged perfectly and previously-dissociated ligand products will adsorb on a clean Ge surface as shown in Figure 2 before any precursor dosing; the red line indicates that around 1 ML equivalent carbon adsorbs on the surface. An MBE-formed Zintl template blocks carbon adsorption (Figure 2). Examination of carbon levels in 2-nm and 10-nm SrZrO<sub>3</sub> films grown on bare Ge indicates the presence of carbon in the 2-nm films suggesting this initial carbon adsorption remains at the interface. Carbon levels in 2-nm and 10-nm SrZrO<sub>3</sub> films grown on 0.5-ML Ba Zintl layers cannot be detected in 2-nm and 10-nm SrZrO<sub>3</sub> films, confirming that the Zintl layer protects the surface from carbon contamination. *In-situ* XPS analysis also shows the MBE-grown Zintl template is relatively unreactive with H<sub>2</sub>O; H<sub>2</sub>O reacts with adsorbed Sr and Zr precursors. The growth mechanism will be discussed during the presentation.

(Figure 1 and Figure 2 are shown in supplemental document)

<sup>1</sup>S. Hu et al., *J. Chem. Phys.* **146**, 052817 (2016).

11:40am **SS-WeM-12 Role of the Surface Charge Density in the Surface Relaxation: The Case of Au(111)**, *M Valbuena*, Universidad Autonoma de Madrid; *C Quiros*, Universidad de Oviedo; *E Salagre*, Universidad Autónoma de Madrid; *A Oliva, M Plaza, J Martinez-Blanco, P Segovia*, Universidad Autonoma de Madrid; *Enrique G. Michel*, Universidad Autonoma de Madrid, Spain

The formation of a surface generates in general a spontaneous contraction of the surface plane to re-establish the equilibrium (surface relaxation) [1]. There are many surfaces where the spontaneous contraction is very small or even it is an expansion instead of a contraction [2]. Interestingly, there are several prominent cases of surfaces exhibiting an anomalous expansion that also present a surface electronic state with a significant density of states [2,3,4,5]. Theoretical calculations have found [3] that the sign and magnitude of the relaxation of the topmost atomic layers of Al(100) is mainly determined by the rearrangements of the surface state charge. In short, the presence of a surface state increases the surface charge density, and this affects the surface relaxation. Analogous calculations show that Au(110) and Au(100) (without a high density of surface states) present a conventional surface relaxation (contraction), while Au(111) (with a prominent Shockley surface state) is characterized by an anomalous expansion [6]. These findings point towards a strong involvement of the density of surface states in the relaxation finally observed.

We report experimental results monitoring directly the change in surface relaxation when the surface charge in the surface state is modified. To this

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end, we tune the Au(111) surface state filling in a controlled way, by depositing suitable acceptor or donor molecular species. Then, we measure the surface relaxation as a function of the surface state charge, using surface x-ray diffraction (SXRD). The SXRD analysis includes the measurement of several Crystal Truncation Rods as a function of coverage of the donor or acceptor species. The results are fitted using standard procedures and provide the surface relaxation. The charge contents in the surface state is also experimentally determined from ARPES measurements of the Fermi contour for different coverages. Our results establish a direct relationship between surface relaxation and charge contents in the Au(111) surface state and shed light on the nature and deep origin of the surface relaxation process.

[1] S.Y. Tong "Surface Crystallography by LEED: Theory, Computation, and Structural Results", Springer.

[2] H.L. Davis et al, Phys. Rev. Lett. 68, 2632 (1992).

[3] V. Chis and B. Hellsing, Phys. Rev. Lett. 93, 226103 (2004).

[4] F. Reinert et al, Phys. Rev. B 63, 115415 (2001).

[5] J. Sun et al, New Journal of Phys. 12, 063016 (2010).

[6] Li Guan et al, Solid. State. Commun. 149, 1561 (2009).

## 12:00pm **SS-WeM-13 Modeling Physical Vapor Deposition of Energetic Materials, Koroush Shirvan**, MIT; *E Forrest*, Sandia National Laboratories

The morphology and microstructure of organic explosive films formed using physical vapor deposition (PVD) processes strongly depend on local deposition conditions, especially the homologous temperature. Given the low melting points of many organic explosives, changes in surface temperature by only a few degrees can result in drastically different explosive morphology and performance. Given the difficulty of accurately measuring surface temperature during energetic material deposition, modeling may provide some insight into local conditions. This work focuses on using a multi-physics computational fluid dynamics tool, STARCCM+, to simulate PVD of pentaerythritol tetranitrate (PETN). The PETN vapor and solid phase are simulated using the volume of fluid method. The deposition fixture, copper cooling block, and assembly rotation are incorporated into the model. Implicit time-dependent simulations in 2D and 3D are performed to derive insight into the governing physics for growth of thin PETN films via PVD.

PETN is deposited at a rate of 0.8  $\mu\text{m}/\text{min}$  at 142.9  $^{\circ}\text{C}$  on a 500  $\mu\text{m}$  thick silicon wafer with an initial temperature of 22 $^{\circ}\text{C}$ . The sublimation of PETN on the wafers is calculated to occur at a heat transfer coefficient (HTC) of 400  $\text{W}/\text{m}^2\text{-K}$ . The HTC for sublimation proved to be the most sensitive parameter in determining the local surface temperature during deposition. Previous experimental studies found noticeable microstructural changes with the use of fused silica wafers of equivalent thickness in place of silicon during the PETN deposition. Effects were likely due to the change in local deposition temperature from the reduction in substrate thermal conductivity. This work confirms the effect, showing that use of fused silica substrates reduces initial wafer cool down and results in  $\sim 10$   $^{\circ}\text{C}$  difference in the surface temperature when depositing a 500  $\mu\text{m}$  thick PETN film. It was also found that the deposition surface temperature is insensitive to the cooling power of the copper block due to the very large heat capacity and thermal conductivity relative to the heat input from the PVD process. Future work will involve incorporation of local stress fields during PETN deposition and cooling.

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