

Surface Energy Controlled Growth of Single Crystalline Two-Dimensional Hexagonal (*h*)-Boron Nitride

Mark H. Griep,¹ Roland Tay,² Travis Tumlin,¹ Govind Mallick,^{1,2} Siu Hon Tsang,² Ram Sevak Singh,² Edwin Hang Ton Teo,² and Shashi P. Karna^{1*}, senior IEEE member

¹US Army Research Laboratory, ATTN: RDRL-WM, Aberdeen Proving Ground, MD 21005

²Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore

*Email: shashi.p.karna.civ@mail.mil

Abstract — Two-dimensional (2D) nanomaterials, including graphene and boron nitride (BN), have been of intense interest in recent years due to their exceptional electronic, thermal, and mechanical properties. Tailoring these novel properties to their maximum potential requires precise control of the atomic layer growth process. In recent years, catalytic growth of 2-D nanomaterials using chemical vapor deposition (CVD) process has emerged as an attractive approach due to their low-cost, scalability, and ability to transfer the grown materials on various substrates. In this approach, the morphology and purity of the catalytic surface plays a critical role on the shape, size, and growth kinetics of the 2D nanomaterial. In this work, we present the results of our systematic studies of the role of catalytic surface morphology on the shape and domain size of CVD grown hexagonal (*h*)-BN films. The present work clearly demonstrates that the presence of surface roughness in the form of ridges leads to a preferential growth of small-domain triangular BN sheets. A 100-fold reduction in the surface roughness leads to increased domain BN triangles, eventually transitioning to large-domain hexagonal shaped BN sheets.

I. INTRODUCTION

Two-dimensional *h*-BN has emerged as an important component in hybrid 2D nanomaterial multi-layered designs. With its highly insulative properties, atomically smooth surface, and closely matched lattice parameters to graphene; *h*-BN has been demonstrated as a key materials in photovoltaic [1], capacitor [2], and high speed transistor applications [3]. As the morphology and purity of the catalytic surface plays a critical role on the shape, size, and growth kinetics of the 2D nanomaterial, and ultimately its physical/electronic properties; optimization of *h*BN growth is an area of intensive study. Chemical vapor deposition (CVD) has emerged as a technique uniquely suited for 2-D material synthesis owing to its controllable process parameters and large area synthesis capabilities. Much research has been dedicated to the CVD process parameters (chamber pressure, temperature, gas exposure time, etc.) effect on 2-D nanomaterial growth; it has also been shown that nucleation and growth of 2-D nanomaterials is highly dependent on the physical properties of the catalytic

substrate. To date multiple methodologies have been explored to increase the control of the active growth substrate surface's grain size, crystal orientation, oxide thickness, exposed functional groups, and surface roughness including tailored annealing, H₂ treatments, controlled oxide growth, etchant pre-cleaning, and electropolishing.

To date, growth of *h*-BN on both Ni and Cu catalytic surfaces has yielded triangular islands of relatively small domain sizes. This consistent morphology has been attributed to the preferential energy state achieved by maximizing the nitrogen-terminated edges; which results in a lower edge energy than a boron-terminated edge [4]. It has been suggested that the formation of a hexagonal *h*-BN island would require alternating nitrogen-terminated and boron-terminated edge structure, thus is an energetically unfavorable structure [5]. Utilizing highly optimized electropolishing protocols, the *h*-BN growth kinetics on ultra-smooth copper were altered in such a manner that resulted in the growth of large single-crystalline hexagonal flake *h*-BN [6].

II. EXPERIMENTAL

Electro-polishing of Cu foil. Copper foils were purchased from Alfa Aesar (25 μ m, 99.8%) and degreased with acetone, IPA, and milli-Q water sequential rinsing prior to use. Copper foil surface tailoring was performed with an electrolyte composed of 330 mL ddI H₂O, 167 mL ortho-phosphoric acid, 167 mL ethanol, 33 mL isopropyl alcohol, and 3.3 g urea. Copper foil sample areas of 5 cm² were electropolished at 8 V under constant flow for the designated polishing time. The as-received samples compared with the electropolished samples are shown in Figure 1. After polishing, samples were rinsed with deionized water followed by a final rinse with IPA. Samples were then dried with a soft stream of nitrogen.

Synthesis of 2D *h*-BN flakes by APCVD. Prior to deposition, the polished Cu foil was dipped in dilute nitric acid for a few seconds to remove the native oxide and rinsed in DI water. 5 mg of Ammonia borane (NH₃-BH₃) was used as a precursor and was placed in a ceramic boat, away from the heating source. The Cu foil was positioned towards the rear end of the quartz tube around 20 cm away from the ceramic boat. Under the protection of 425 sccm of Ar and 75

sccm of H_2 , the Cu foil is annealed at 800 °C for 20 min and then raised up to 1050 °C in 40 min. During growth, the temperature was kept at 1050 °C for 30 min and ammonia borane was heated up by a flexible heating belt at 60 °C. At the same time, the gas flow of Ar and H_2 is reduced to 170 sccm and 30 sccm respectively. At the end of the growth, the gas flow of Ar and H_2 were set back to 425 sccm and 75 sccm, respectively, and the lid of the furnace was lifted for fast cooling.

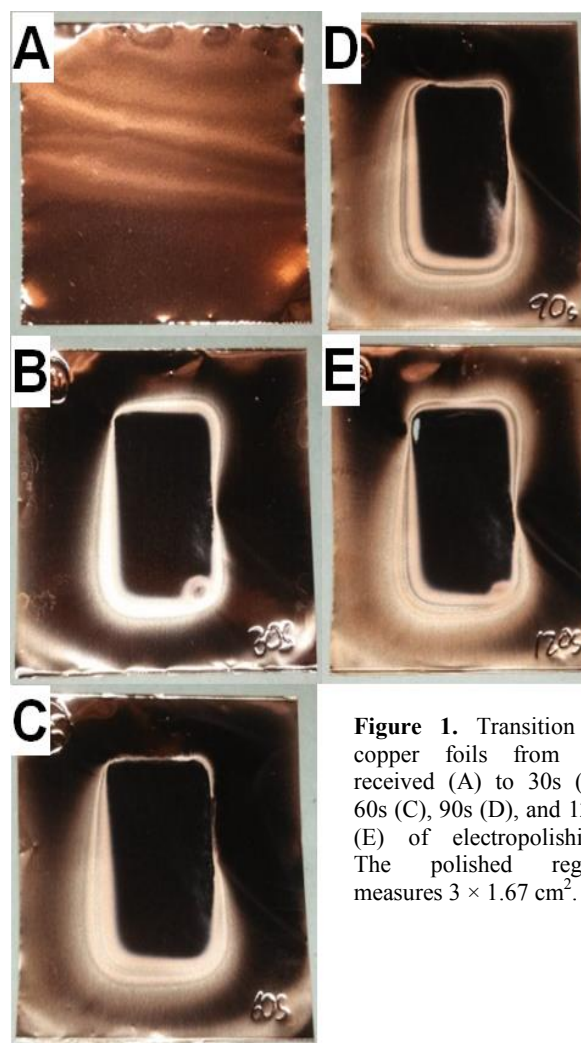


Figure 1. Transition of copper foils from as-received (A) to 30s (B), 60s (C), 90s (D), and 120s (E) of electropolishing. The polished region measures $3 \times 1.67 \text{ cm}^2$.

III. RESULTS AND CONCLUSIONS

Ultra-smooth copper substrates, as shown in Figure 2, were prepared at multiple roughness levels to systematically study the role of roughness on precursor surface diffusivity and *h*-BN nucleation density. Optical profilometry was performed to characterize the change in surface roughness, as shown in Figure 3, with respect to polishing time. Optimized electropolishing conditions allowed for reductions in surface roughness of up to 99.28% compared to the control foils, as shown in Figure 4, which is far beyond that

currently reported in literature. Polishing copper foils beyond 120s increased surface roughness due to excess pitting; further polishing of the sample led to rapid disintegration of the polished region thus only samples polished under 150s were prepped for 2-D nanomaterial growth. At each roughness level, alterations in the *h*-BN domain were induced, with increased triangular flake sizes at the 30s and 60s electropolishing timepoints, followed by transition to hexagonal flakes at 90s, as shown in Figure 5. It was also determined that the nucleation density of the *h*-BN was reduced as polishing time was increased. This is thought to be a result of the reduction in potential nucleation sites which include surface striations and impurities. The synthesized hexagonal shaped *h*-BN were determined to be single crystalline in nature, as opposed to coalesced triangular flakes, and yielded sizes flake domain sizes up to $35\mu\text{m}^2$. The increase in domain size occurred in conjunction with a nearly 10-fold decrease in nucleation density, again,

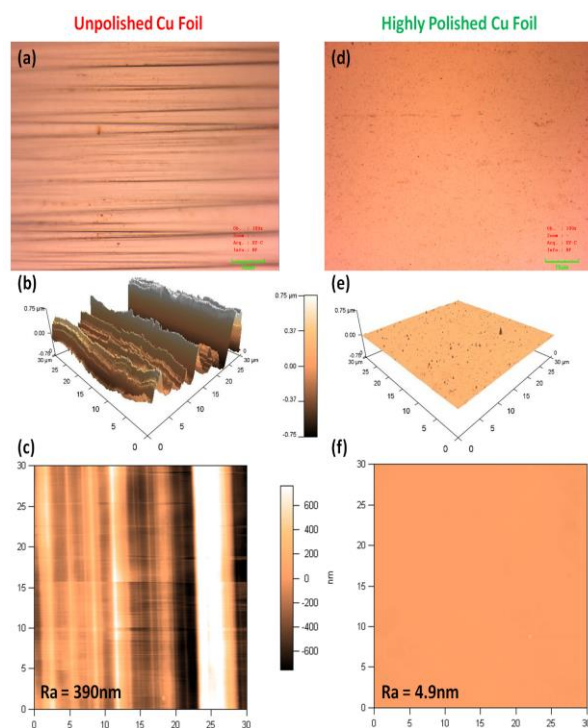


Figure 2. Electro-polished Cu foils. Optical micrographs and AFM images, with the height profile in the inset, on (a, b, c) unpolished Cu foil, and (e, f, g) highly polished Cu foil after 90 s of polishing time respectively.

due to the decrease in nucleation sites at sharp topographical features. After deposition, samples were transferred onto SiO_2 for further characterization as shown in Figure 6. Although a full kinetic model has yet to be established to explain the decrease in nucleation density, it is hypothesized that the decrease in surface roughness increases the surface energy. This increase in surface energy then leads to an increase in Gibbs free energy. This overall increase in surface energy thus reduces the number of sites that are energetically favorable for *h*-BN nucleation.

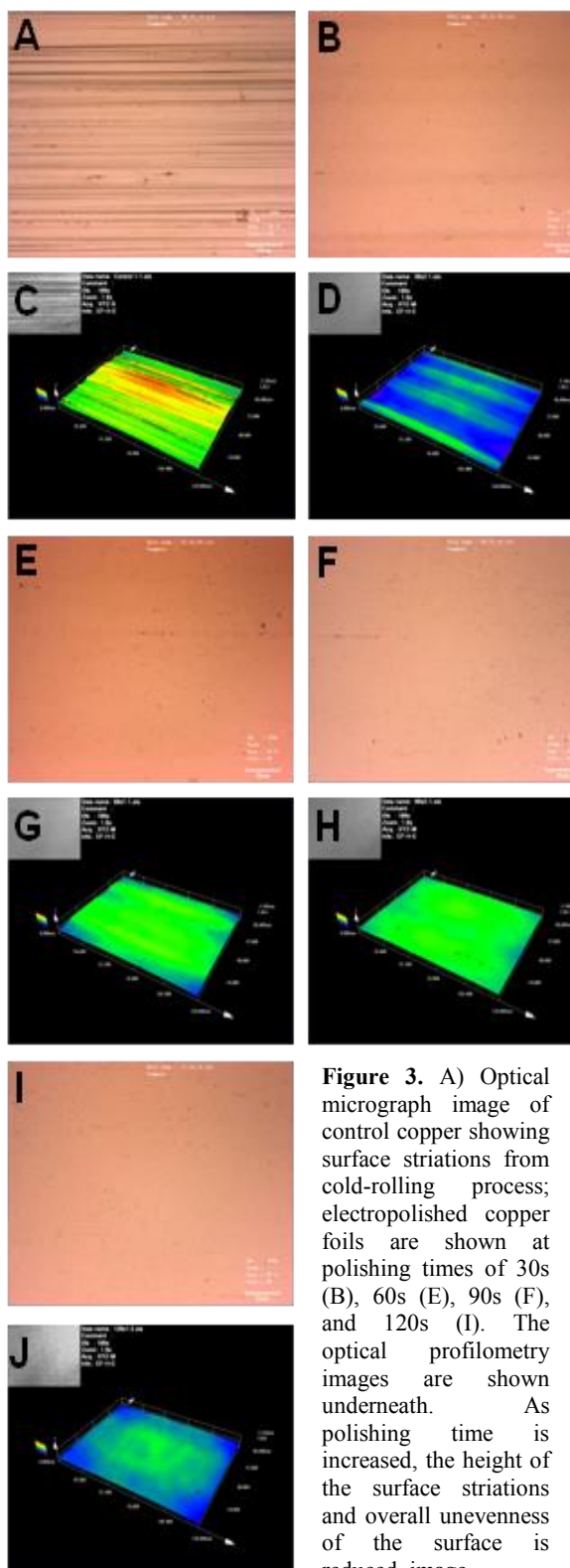


Figure 3. A) Optical micrograph image of control copper showing surface striations from cold-rolling process; electropolished copper foils are shown at polishing times of 30s (B), 60s (E), 90s (F), and 120s (I). The optical profilometry images are shown underneath. As polishing time is increased, the height of the surface striations and overall unevenness of the surface is reduced. image.

A recent study showed that surface oxygen content plays a large role in both the shape and domain size of graphene [7]. It was determined that oxygen aids in the edge dehydrogenation which is thought to reduce the edge energy attachment barrier thus accelerating graphene growth. In the present work, it is suspected that the oxygen content of the

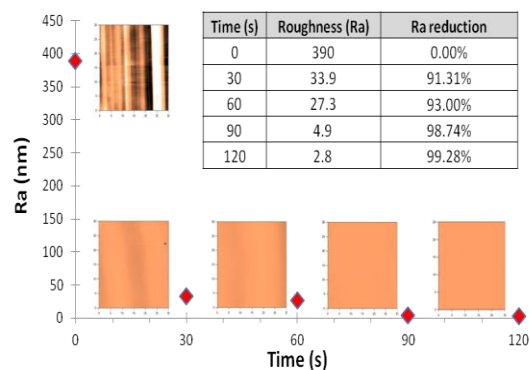


Figure 4. Tracking of AFM Ra analysis versus electropolishing duration. Inset images correspond to AFM topographical map at each timepoint.

electropolished copper plays a similar role by removing the attached hydrogen thus allowing both boron and nitrogen species to attach. XPS studies were carried out to determine the oxygen content in both the polished and unpolished copper foils.

It was determined that electropolishing the surface leads to an increased amount of surface oxygen due to the interaction of the phosphoric acid (H_3PO_4) electrolyte with the Cu surface. This interaction leads to the formation of surface oxygen species in the forms of Cu_2O , CuO , and $Cu(OH)_2$ [8]. The added oxygen content of the surface reduces the edge energy attachment barrier enough for the *h*-BN to have both nitrogen and boron terminated edges leading to hexagon shaped domains. It is also suspected that the reduced roughness allows BN radicals to diffuse more freely across the copper surface thus facilitating the growth of larger domain

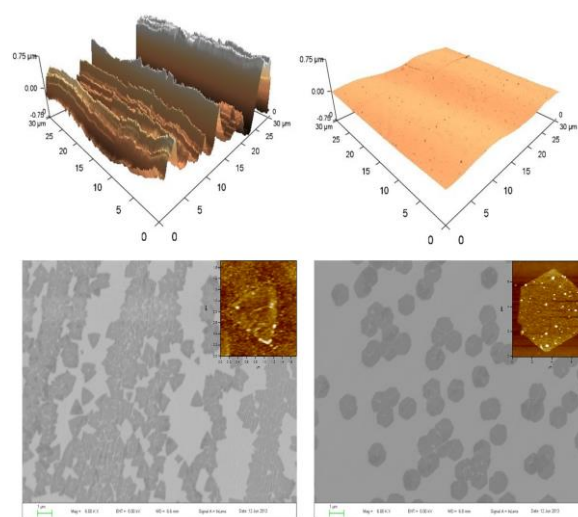


Figure 5. Catalytic substrate roughness directs the nucleation and growth parameter of CVD-grown Boron Nitride (a) triangular or (b) hexagonal BN domains.

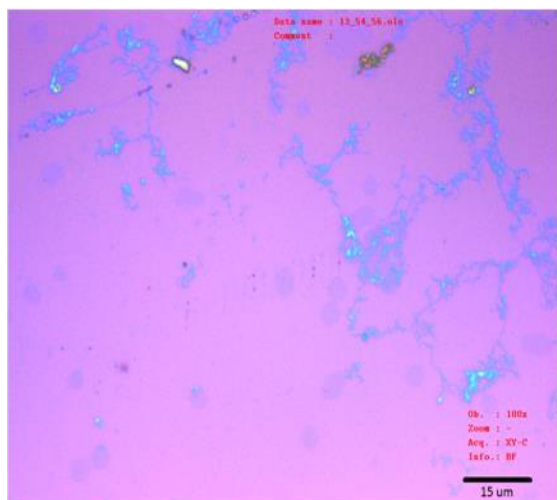


Figure 6. Optical micrograph showing hexagon shaped domains transferred onto SiO₂. Note the contrast between the monolayer *h*-BN hexagons and the oxide layer. The blue portions of the image are undissolved polymer residue.

Atomic force microscopy (AFM) characterization of the hexagon shaped flakes, as shown in Figure 7, showed a step height suggesting that the domains were not a single layer. This is likely due to the AFM tip having greater interaction with the SiO₂ layer than with the *h*-BN. This

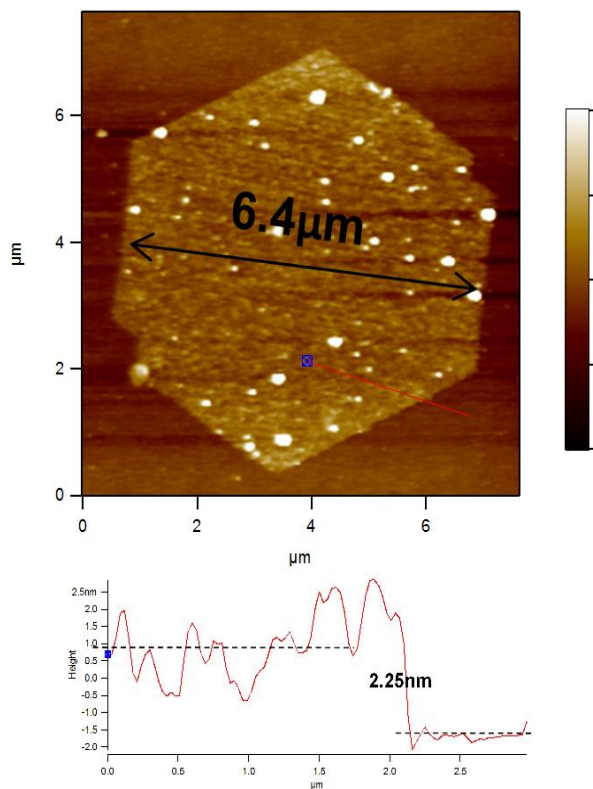


Figure 7. AFM of large individual domain with length of 6.4μm and thickness of 2.25nm.

increased interaction yields experimental measurement values that do not always agree with theory. Similar AFM

results have also been reported for graphene step height [9,10]. It is thought that the *h*-BN interaction is similar to that of graphene thus leading to erroneous step height values. Enhanced quality of the *h*-BN film in terms of monolayer full-film production and improved film surface roughness will be presented in addition to a detailed substrate kinetics evaluation.

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