Advancing Semiconductor Manufacturing through DNA-Templated Lithography and Molecular-Scale Patterning of 2D Materials

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***Abstract*— This paper explores the potential of using DNA nanostructure to pattern molybdenum disulfide (MoS_2) for potential applications in nanoelectronics. We developed a gas phase synthesis of MoS_2 with minimal out-of-plane growth and low defect density. We used density functional theory (DFT) calculation to examine the bandgap modulation of MoS_2 due to counterion diffusion from DNA, highlighting the electron transfer mechanism during lithium intercalation. Lastly, we demonstrate deposition of DNA triangles and nanotubes on various MoS_2 surfaces. Contrary to previous results, we found that these DNA nanostructures maintained their structural stability. These findings collectively contribute valuable insights into using DNA nanotechnology to advance 2D electronics.**

Keywords—DNA origami, MoS_2, 2D materials, nanoelectronics, doping

I. Introduction

The exponential growth of integrated circuits, integral to modern technologies, have faced challenges in recent years due to the increasing difficulty of lithographically patterning silicon with a pitch smaller than 25 nm using optical lithography. This limitation has spurred focused research on engineering innovative materials and patterning methods for electronic devices. The current reliance on Si-electronics poses significant challenges in terms of scalability, underscoring the critical necessity for a new material system in electronics.

In addressing these challenges, one promising research direction is the integration of molecular-scale patterning and doping into atomically thin materials like graphene and MoS_2, utilizing DNA-templated lithography masks. This approach has the potential to overcome challenges in traditional lithography (sub-25 nm pitch) and address the quest for a new computing paradigm.

Liu and Xiong have recently introduced an innovative technique for silicon (Si) doping, utilizing DNA nanostructures as a dopant source[1]. Through their method, they demonstrated that, under elevated temperatures, phosphorus atoms from the DNA diffuse into the silicon wafer, leading to the creation of n-doped regions. The spatial distribution of dopant atoms is determined by the shape of the DNA nanostructure, showcasing sub-50 nm resolution in their experiments. Utilizing individually doped regions, field-effect devices were successfully fabricated, confirming the effectiveness of their n-doping approach. On other hand, in prior experiments, Liu observed the co-deposition of positively charged counter ions (e.g., Mg^{2+}) when depositing a DNA nanostructure on a solid substrate. Remarkably, the shape of these DNA nanostructures remains unchanged even under harsh conditions, such as heating to 200 °C, showcasing their enhanced stability compared to solution counterparts[2]. Importantly, even after removing DNA nanostructures through thermal or UV-Ozone oxidation, the counter ions persist undisturbed on the substrate and maintain its nanostructure shape.

Based on this prior work, we hypothesize that DNA nanostructure can assemble ionic intercalants and deliver these ions to a 2D material surface with nanometer precision. Counterions significantly influence the charge transport in DNA, as evidenced by our previous research [3]. Similarly, the electronic properties of MoS2 are influenced by counterions, as indicated by various doping studies [4, 5]. The selection of ionic intercalants depends on factors such as (a) the likelihood of the counterion binding to DNA and (b) the probability of the counterion diffusing into the MoS_2 film. Previous studies have demonstrated that cations tend to bind to guanine bases in the major groove or to oxygen atoms in the phosphate group. These binding sites are readily

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exchangeable, allowing a wide range of cations to be accommodated. In this study, we will investigate the doping effects of both small cations like Li and large cations such as Eu. By carrying these charges to the surface of MoS_2 via DNA origami, we anticipate achieving selective doping on the MoS_2, particularly in regions where DNA origami is present, using solid-state ion exchange. With this work we ultimately want to develop optimum 2D material-based analog memory with specific characteristics such as precision (>1000 resistance levels), low switching energy (<5 aJ/switching), high speed (<10 ns), large dynamic range in resistance (>1000× on/off ratio), linear and symmetrical responses, and high endurance (>108 cycles). The research aims to develop a new synaptic device paradigm by modulating the conductance of 2D analog memory devices to mimic synaptic plasticity. The integration of DNA nanostructure patterning and doping is expected to enable the control of the number of point defects in 2D devices, which in turn can modulate intercalant concentration and intercalation speed, thus engineering the device dynamic range in resistance, precision, and operating speed. Here, we discuss preliminary, yet promising results that indicate the feasibility of the proposed DNA based doping of 2D materials.

II. Literature Review of MoS_2 Doping Using DNA

DNA doping represents an unconventional doping method for MoS_2, blending biomedical technology with nanotechnology. In 2014, Park et al. introduced synthesis methods for artificial DNA and metal-modified DNA (M-DNA), involving metal ions like Zn^{2+}, Ni^{2+}, Co^{2+}, or Cu^{2+}, and their application in doping MoS_2[6]. The study explored the doping of MoS_2 using artificial DNA (n-type) and M-DNA (p-type), revealing a non-degenerate doping effect on MoS_2 films. It is suggested that the phosphate sites in DNA backbones trap hole carriers at the DNA-MoS_2 interface, leading to n-type doping of MoS_2 layers. Conversely, M-DNA, with metal ions, possesses positive dipole moments that reduce electrons in MoS_2 thereby inducing p-doping in MoS2 films. In 2016, Kang et al. demonstrated the feasibility of achieving ultra-low n- and p-doping of MoS_2 down to intrinsic levels by selectively or combining different types of cations introduced by DNA nanostructures[7]. Initially, DNA nanostructures were functionalized with either a divalent or trivalent ion, followed by deposition on mos2 surfaces. For MoS2 devices doped with Ln-DNA, the authors observed an increase in the electric field at the Ti-MoS_2 junction on the source side due to the downward shift of the MoS_2 band. This facilitated the injection of electrons from Ti to MoS_2, leading to a decrease in threshold voltage. In the MoS_2 device co-doped with Cu^{2+} and Eu^{3+} or Gd^{3+}, the energy band of MoS^2 moved upward, reducing the electric field at the source side junction and increasing the effective electron barrier height, resulting in a positive shift of threshold voltage. By delivering target doping ions via DNA nanostructures, this method could offer arbitrary doping patterns within one step, albeit limited to dopant sources capable of binding with DNA.

III. Experimental

A. Monolayer MoS_2 synthesis

Molybdenum hexacarbonyl and hydrogen sulfide were used as precursors and deposited on c-plane sapphire by metal organic chemical vapor deposition (MOCVD). The MOCVD system used is composed of a cold walled quartz tube chamber with an inductively heated SiC-coated graphite susceptor that produces fully coalesced transition metal dichalcogenide films (TMD) across a 2-inch wafer. The susceptor features gas foil rotation to ensure sample uniformity across the entirety of the wafer. The growth process consists of a pre deposition anneal step in a hydrogen atmosphere and minimal flow of the hydride precursor. This step forms ordered terraces on the sapphire surface while also stripping dangling oxygen bonds on the wafer surface. The dilute amounts of sulfur can also fill vacancies on the sapphire basal plane. All this contributes to a more controlled nucleation of the 2D material. After the pre-anneal step the metalorganic precursor is introduced to start nucleation and growth. Once the growth is complete a post-growth anneal is conducted again using the hydride precursor and hydrogen carrier gas. This step allows for vacancy filling in the TMD basal plane. Upon removal from the reaction chamber, we characterize the coverage and quality of the deposited films. Atomic Force Microscopy (AFM) is used to determine layer coverage. Monolayer coalescence is confirmed using Raman spectroscopy, where the separation of the two prominent Raman modes correlate to the characteristic in plane and out of plane vibrations of the layer. The separation of these two peaks directly correlates to the layer number of the deposited sample[8], [9]. Additional layers can then be visualized by AFM. Quantification of layer coverage above the monolayer is accomplished by an image processing technique using FIJI. In this technique the AFM image is converted to grayscale and methodically segmented into bins. The resulting histogram is used to generate a binary mask using an ISO Data thresholding method, yielding a percent contribution to the total image.

B. Bulk and multilayer MoS_2 preparation

Fresh multilayer and bulk MoS_2 samples were prepared using MoS_2 crystals obtained from SPI supplies. To prepare bulk MoS_2, the process involved utilizing scotch tape to peel thin layers from the MoS_2 crystal, while for multilayer MoS_2 (5 - 6 layers), a sequential peeling approach was employed. Specifically, a single tape was used to repeatedly peel the

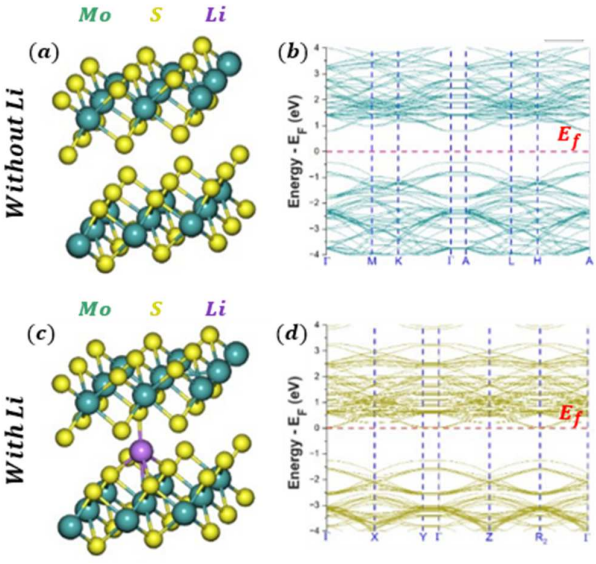


Fig. 1. 3×3 MoS2 supercell (a) without and (c) with Lithium (Li) intercalated atom leading to change in bandgap modulation as can be seen in (b) & (d) for the two cases. The Fermi energy (E_f) is shown in red dotted line. The K-path calculations has been computed according to [13].

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small crystal until the tape was fully covered with MoS_2 flakes. The tape was then placed onto a Si wafer and pressure was applied to induce the transfer of MoS_2 flakes to the wafer. Multilayer MoS_2 was confirmed using AFM.

C. DNA origami synthesis, deposition on MoS_2 and doping

DNA triangle and DNA nanotube was synthesized based on previous reports [10, 11]. To study the deposition of DNA origami on MoS_2, 20 µL (5 ug/mL) DNA triangle nanostructure was deposited on MoS_2 and left undisturbed for 30 minutes. After 30 minutes the sample was washed with 90:10 ethanol: water mixture and analyzed using AFM. Bulk MoS_2 samples were analyzed without washing. After the samples were dried using stream of N_2, the samples were kept in a furnace and heated to 500 °C for 1 hour and then imaged using Kelvin probe force microscopy (KPFM) to confirm the doping of MoS_2.

IV. Result and Discussion

A. MoS_2 characterization

We observed significant bilayer coverage occurs while achieving wafer scale coalescence with minimal multilayer (3+ layers) and out of plane growth. Out of plane growth occurs when nucleated domains grow into each other and begin growing normal to the basal plane rather than properly ripening into a smooth flat film. Samples used in this study averaged 27% Bilayer coverage with less than 2% multilayer/out of plane coverage. Raman spectroscopy was also used to get a qualitative understanding of the defect nature of the 2D material. Raman maps (50 µm in size) were taken at multiple points on the wafer surface. The characteristic in-plane and out-of-plane Raman peaks from the spectral maps were analyzed as well as checking for the presence of the defect associated LA(M) peak [12], [13]. Samples produced for this study lacked this LA(M) peak which is evidence of a low defect density. This low defect density along with the limited amounts of multilayer regions indicate that these TMD samples have a pristine basal plane making them ideal candidates for doping using DNA nanostructures.

B. Simulation study of MoS2 bandgap modulation

When the DNAs are kept at high temperature on the surface of 2D materials, counterions are diffused into the 2D film, modulating its bandgap and subsequently leading to variation in transport properties. To study this band gap modulation, first-principal calculations have been carried out in Quantum-Espresso DFT package [14]. For all atoms, ultrasoft pseudopotentials have been used [15]. The 3×3 MoS_2 supercell without and with a single lithium atom is shown in Figure 1(a) and (c) respectively. The first step in the simulation involves a gamma point relaxation of both the structures. Due to the large size of the system and limited computational resources, relaxation has been done with a gamma point calculation. However, for the band calculations, we have chosen a highly dense K-mesh. The K-path for each structure has been computed according to [16,17]. Both force and electron convergence threshold for system optimization have been considered to be 1×10^ (-5) eV/Å. A degauss value of 0.002 has been used. The energy cutoff is chosen to be 700 eV. To negate the impact of vertical supercell, a vacuum 20 Å is considered. From previous works [18], it is known that DFT cannot estimate the van-der Waals forces effectively, thus a van-der Waals correction model ('grimme-d3') [19] has been invoked in the simulation setup. The band structures of the system without and with Lithium are shown in Figure 1(b) and 2(d). It can be noticed that the Fermi energy lies almost in the middle for the case without any intercalation, while it shifts towards the conductance band during Li intercalation. The reason can be attributed to the donation of electrons by Li atom. For deeper insights, we have performed a fat band analysis to understand the contribution of different orbitals in bandgap determination. It has been found that the d-orbitals of Molybdenum (Mo) and p-orbitals of Sulphur (S) contributes majorly while minor contribution comes from s-orbitals of Lithium (Li), asserting the transfer of electrons between Li and MoS_2 layer.

C. DNA origami stability on MoS_2 and doping

We observed stable DNA triangle and DNA nanotube deposition on monolayer, multilayer and bulk MoS_2 surfaces.

The structures were confirmed by AFM and KPFM. Our results differ from the previously reported deformation of DNA origami on MoS_2 [20]. The DNA origami used in their study was seen to undergo severe deformation after being deposited on freshly exfoliated MoS_2. We believe this is due to greater structural stability of DNA triangle and nanotube used in this study.

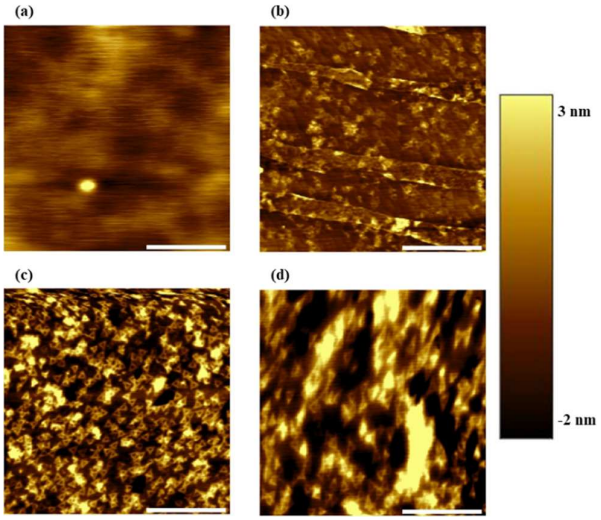


Fig. 2. AFM image showing DNA triangle deposited on different MoS_2 surfaces (a) monolayer MoS_2 (b) DNA triangle deposited on monolayer MoS_2 (c) DNA triangle deposited on bulk MoS_2 and (d) DNA triangle deposited on multilayer MoS_2. Scale bars indicates 1 µm.

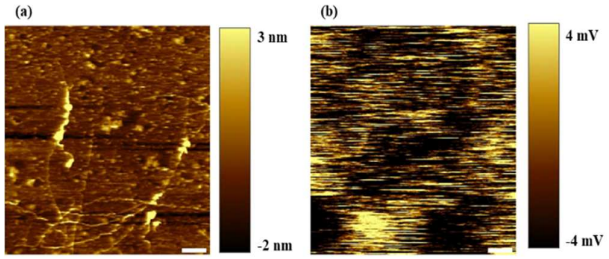


Fig. 3. KPFM image showing height trace and the potential trace of DNA nanotube deposited on Monolayer MoS_2 (a) Height trace of DNA nanotube deposited on monolayer MoS_2 (b) Potential trace of DNA nanotube deposited on monolayer MoS_2. Scale bars indicates 1 µm.

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Initial KPFM imaging of DNA nanotube confirms its presence on potential image Figure 3(b). Work is underway to evaluate the possibility of incorporating Mg^{2+} into MoS_2 lattice.

V. Conclusion and Future Direction

In conclusion, these findings collectively contribute valuable insights into possible integration of DNA nanotechnology with 2D electronics. The successful synthesis and characterization of MoS_2, simulation study providing insights into bandgap modulation induced by counterion diffusion from DNA, coupled with initial success of integrating DNA templates with MoS_2, open avenues for the development of novel materials and patterning methodologies in semiconductor manufacturing.

It is to be noted that the results reported here are only preliminary. Work is underway to study the doping of magnesium and/or other metal cation into MoS_2. We plan on working towards this and confirm the doping of MoS_2 using KPFM. Although we believe these results can spur future experimental research, there are a lot of open questions that need to be addressed. For instance, we are working on improving the doping accuracy on MoS_2 by considering several counterions. The counterions will be selected based on binding strength to DNA and diffusion coefficient on MoS_2 surface. From a computational standpoint, we plan to intercalate a variety of counterions to understand their impact on the electronic structure of MoS_2. We also intend to increase the size of our system to negate the effect of very high doping density. The flat band analysis will be extended to a tight binding model to compute transport properties.

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