

Advanced EUV patterning of 2D TMDs for CMOS integration

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ABSTRACT

Field-effect transistors (FETs) with channels of two-dimensional transition metal dichalcogenides (2D TMDs) are expected to extend Moore's law by extreme scaling of contacted gate pitch (CGP) post silicon-sheet-based complementary FET (CFET) devices. The ultrathin body and fully passivated surface of 2D materials result in superior electrostatic control and improved short channel behavior [1].

Challenges such as high contact resistance or lack of doping technology are on the way of 2D-FETs reaching the required performance for high-performance logic applications [2,3]. Additionally, in order to integrate 2D TMDs in ultra-scaled CMOS devices, developing a patterning scheme via the state-of-the-art extreme ultraviolet (EUV) lithography is essential [4].

In this paper we demonstrate our first results on studying the compatibility and interaction of semiconducting 2D TMDs with EUV environment using a set of characterization techniques that are fit to detect qualitative defects and morphological changes in these atomically thin layers. Our study is focused on semiconducting TMDs that are currently the most promising candidates for transistor channels: MoS₂ (NMOS) and WSe₂ (PMOS). We report the interaction of EUV photons and photo-electrons with blanket films of MoS₂ and WSe₂ for different EUV doses in vacuum environment. Based on the current findings we propose design of experiments aiming at developing controllable and tunable modification and patterning of 2D TMDs with the EUV energy and resolution for advanced device nodes.

Keywords: 2D materials, defect characterization, transition metal dichalcogenides, area-selective, EUV

1. INTRODUCTION

Extension of Moore's law towards advanced device nodes relies on technological innovations in multiple directions. Incorporating novel materials and integration schemes with new device concepts enable placing more transistors per unit area while improving the overall performance.

Field-effect transistors (FETs) with channels of two-dimensional transition metal dichalcogenides (2D TMDs) are expected to extend Moore's law by extreme scaling of contacted gate pitch (CGP) post silicon-sheet-based complementary FET (CFET) devices. The ultrathin body and fully passivated surface of 2D materials result in superior electrostatic control and improved short channel behavior. [1]

To achieve full wafer integration of aggressively scaled 2D-based logic circuits, multiple performance and fabrication challenges must be overcome. The most essential areas that need additional attention are reducing contact resistance, developing stable and controllable deposition and doping schemes for channel, source/drain and the gate oxide/metal regions. Additionally, developing a patterning scheme via the state-of-the-art extreme ultraviolet (EUV) lithography is a required step in order to achieve extremely scaled 2D-FETs [2,3].

At the moment fabrication of 2D-FETs with channel dimensions smaller than few hundred nanometers on a 300 mm wafer is very challenging due to lack of adhesion forces at the surface and low mechanical stability of these layers. During the dry etch process, the dangling bonds on the side of 2D layers interact with the photoresist and leave the patterned area with residues and very rough edges. Based on previously published research articles, the energetic particles that are present in the EUV environment (photons with energy of 92 eV energy, primary and secondary electrons with energy of few to tens of eV, and H₂ plasma species) have the potential to interact with TMD layers with bond energies of few electron volts, resulting in local modification of the layers e.g. creating defects or local annealing that might hinder the final device performance [5].

Fundamental understanding of EUV interaction with 2D layers, developing a customized and EUV compatible patterning strategy combined with dry-processing steps for active area and contacts could facilitate scaling the device dimensions down to achieve the sub 10 nm gate length. However, a local, tunable and controllable annealing or defect creation scheme upon EUV irradiation could act as an enabler for a directed and area-selective processing of these layers e.g. EUV-induced etching or improved contact resistance by locally annealing or doping the 2D layer at the source/drain spacer region. [6,7]

Figure 1.a is a schematic of EUV environment; where photons at wavelength of 13.5 nm and energy of 92 eV arrive at the substrate (wafer) and generate photo electrons with energies below 92 eV as well as secondary electrons, with highest distribution around energies below 20 eV, similar to the case in scanning electron microscope (SEM). Monte-Carlo simulations provide mean free path, energy and spatial distribution of secondary and backscattered electrons (figure 1.b). The absorption ratio of EUV photons and secondary electron yield depend on the elemental composition of the substrate (figure 1.c).

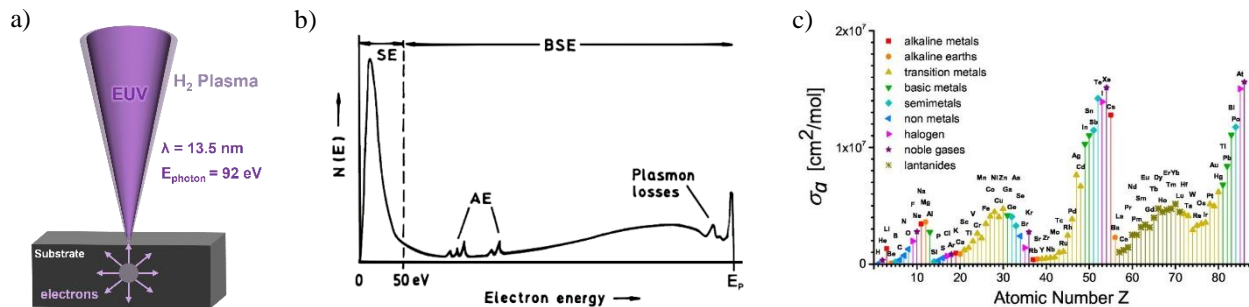


Figure 1 a) Schematic of EUV environment close to wafer b) energy distribution of emitted electrons from the sample in SEM obtained by Monte-Carlo simulations [8] c) atomic absorption cross-section (σ_a) at EUV wavelength ($\lambda = 13.5$ nm) of elements with atomic number Z [9].

In addition to photons and electrons, low pressure hydrogen (H_2) in the vicinity of EUV leads to ionization of H_2 and creation of a plasma that extends several centimeters beyond the EUV beam [10,11]. There are several reports on the modification on 2D layers (etching, doping, inducing strain,...) using plasma environment [12,13].

2. EXPERIMENTAL DETAILS

The key semiconducting candidate materials for transistor channel with expected higher mobilities and chemical stability are MoS_2 (NMOS) and WSe_2 (PMOS). To study interaction of EUV environment with TMD layers, we start with exposing blanket films of MoS_2 and WSe_2 grown on different substrate to EUV photons in vacuum. For this study it is essential to dissociate the impact of different energetic particles from each other. The first set of experiments are done in vacuum and in the absence of any plasma environment.

The EUV light in the research setup (figure 2.a) is generated using a gas discharge source, filtered and then focused on the sample plane 1.5 meter away from the source. The beam has a gaussian shape, with peak intensity covering a disk area with a diameter of ~ 3 mm (figure 2.b&c). With a fixed incident dose of 300 mJ/cm² per second, a combination of attenuation filters (10%, 1% and 0.1%) and various exposure time are used to illuminate the samples with different exposure doses.

The key advantages of this system include 1) having access to the same wavelength (13.5 nm) and energy of photons (92 eV) as in the EUV scanner, 2) a large area point exposure which is compatible with defect characterization techniques (RAMAN, PL or XPS) where an area of few hundreds of microns up to few millimeters is being studied, 3) due to the gaussian shape of the beam, various doses land on the same surface and it is possible to study areas exposed to different exposure doses on the same sample, 4) upon insertion of H_2 , N_2 or O_2 in the chamber it is possible to study the impact of environment e.g. plasma on the sample.

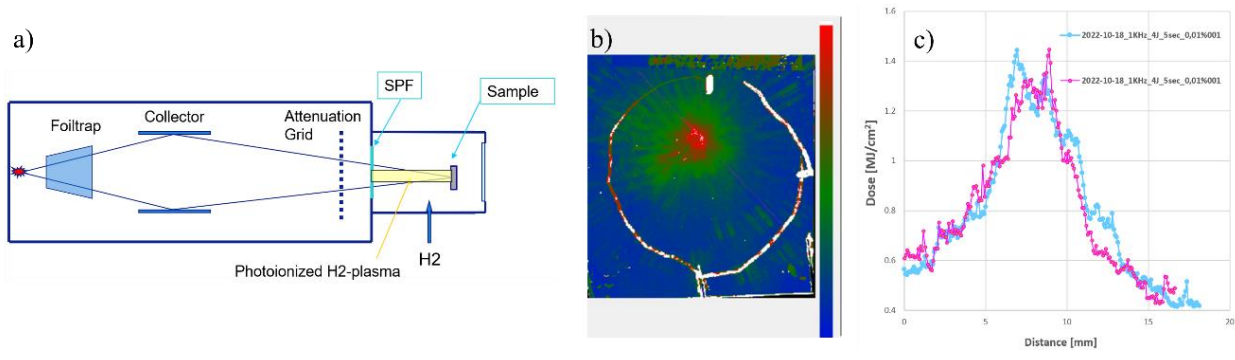


Figure 2 a) drawing of the EUV research setup, b) re-colored photo of the transparent film used to locate different EUV intensities at the sample plane, c) two measured gaussian distributions of the EUV intensity superposed

2.1 MoS₂ on Sapphire

Films of two-dimensional Molybdenum disulfide (MoS₂) are grown on sapphire wafer via metal organic chemical vapor deposition (MOCVD). Atomic force microscopy (AFM) images of as grown films confirm a closed monolayer with polycrystallinity in nature (confirmed by GIXRD), islands of second layer are also present on the sample (figure 3). Raman spectroscopy measurements at room temperature and at 78 kelvin confirm the crystalline structure of MoS₂ and the expected number of layers. With increasing number of single layers, the in plane E_{2g} mode at ~383 cm⁻¹ shifts to lower frequencies and the A_{1g} mode at ~408 cm⁻¹ shifts to higher frequencies (figure 4)

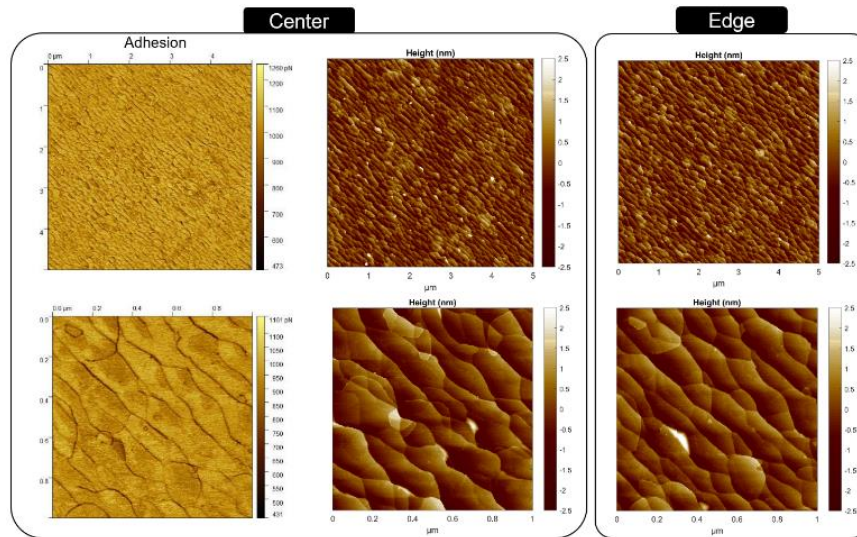


Figure 3 – Height and adhesion channel of AFM (peak-force based) images of as grown MoS₂ on 2 inches sapphire wafer, acquired from center and edge.

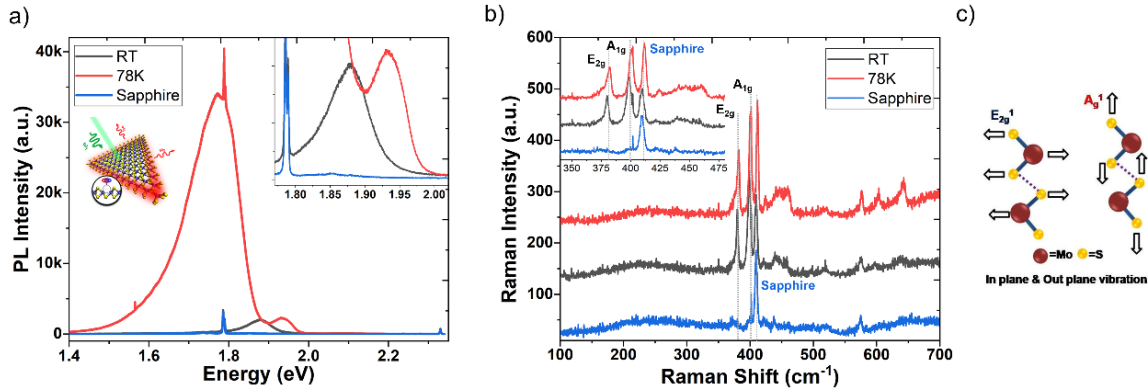


Figure 4 a) Cryo-photoluminescence (PL) response of as grown MoS₂ films on sapphire, a broad defect-bound exciton peak appearing at low temperature ~1.8 eV, b) RAMAN spectra of as grown MoS₂ film on sapphire measured at room temperature (RT) and at 78 kelvin. c) observation of any change in-plane vibration E_{2g} @385 cm⁻¹ and out of plane vibration A_{1g} @ 405 cm⁻¹ after EUV exposure could be linked to induced strain, wrinkling, delamination, etc.

The appearance of broad peak centered at ~1.8eV in cryo-photoluminescence measurement, is linked to the energy of defect-bound excitons. The integral intensity of this peak is linked to density of defects present on the area of the 2D layer covered by the laser. These defects could represent a chalcogen/metal vacancy, or absorption of a foreign atoms e.g. oxygen at the defect site [14,15].

As grown MoS₂ on sapphire wafer was cleaved into 6 coupons, two of the coupons act as control samples. One staying at the original location (imec) and the other one with the remaining four coupons travel to ASML where the EUV exposure takes place. Due to the very high sensitivity of 2D films to air (oxygen, humidity) and light, it is crucial to store and transfer the samples in vacuum and away from light. The samples get exposed to ambient conditions for few minutes during the load/unload in EUV chamber and characterization setups.

During the first round of experiments, we transferred the samples without vacuum packing. The photoluminescence measurements on all samples (exposed and control) pointed to a fully passivated surface and absence of the defect peak at ~1.8 eV, while the control sample at imec did not go through that change (figure 5). Once the samples were vacuum transferred, we could measure back the defect peak which indicates that few minutes of exposure to air during load/unload has minor (negligible) effect on the existing defect state of 2D MoS₂ films.

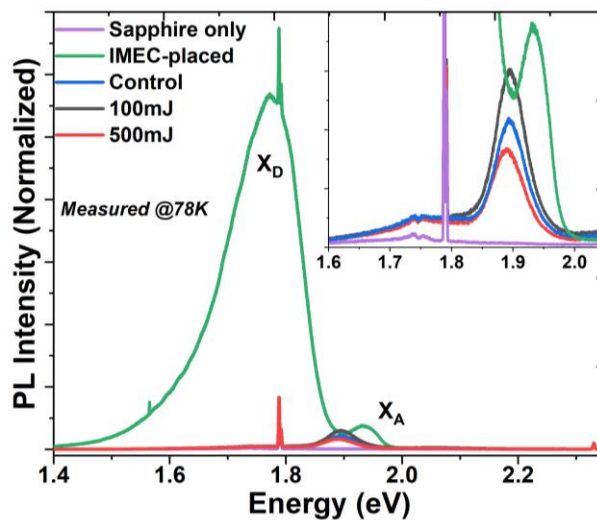


Figure 5 – Cryo-PL response of the MoS₂ samples at 78 kelvin, defect peak has disappeared (suppressed) highlighted in inset for all travelling samples due to surface passivation by humidity except for the one staying back in imec.

Samples were exposed to various doses of EUV light in vacuum. An EUV dose of around 300 mJ/cm² in the research setup is obtained upon 1 second of exposure without any attenuation filters using a manual shutter. Higher doses are obtained via longer exposure times e.g. a dose of 5 J/cm² is reached via an exposure time of 17 seconds.

Figure 6a-c shows the sample (camera-clicked picture) placed on the sample holder, where the surface of the sample is fully exposed to EUV photons, and the peak intensity arrives in an area with a diameter of 3 millimeters at the center of holder.

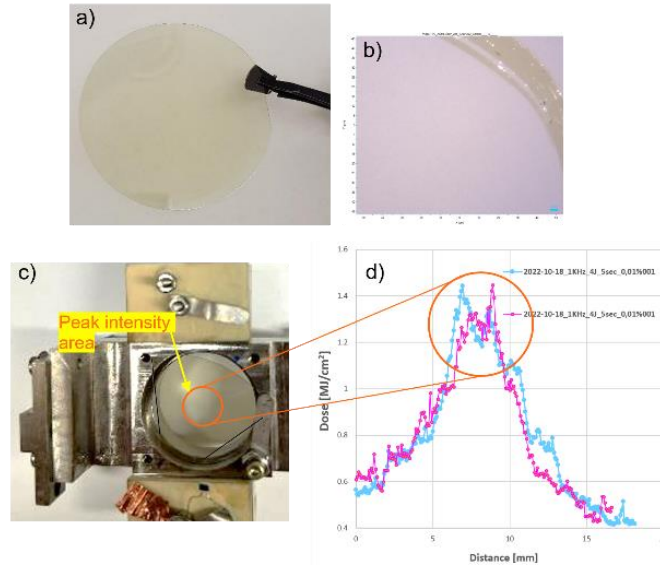


Figure 6 a) Camera clicked picture of the monolayer MoS₂ uniformly grown on 2” sapphire wafer in an industrial MOCVD reactor, and corresponding b) optical micrograph of the MoS₂ surface (top right corner shows the manually scratched region), c) photo of the MoS₂ on sapphire sample on the EUV sample holder, d) the gaussian distribution of EUV dose connected to the area on the sample

EUV-exposed films of MoS₂ were vacuum transferred and characterized at imec, no morphological damage was observed by optical microscope examination. RAMAN measurements do not show signs of strain, wrinkling or delamination even at very high dose (5 J/cm²). This was also backed-up by AFM images at both higher and lower doses (figure 7a-c).

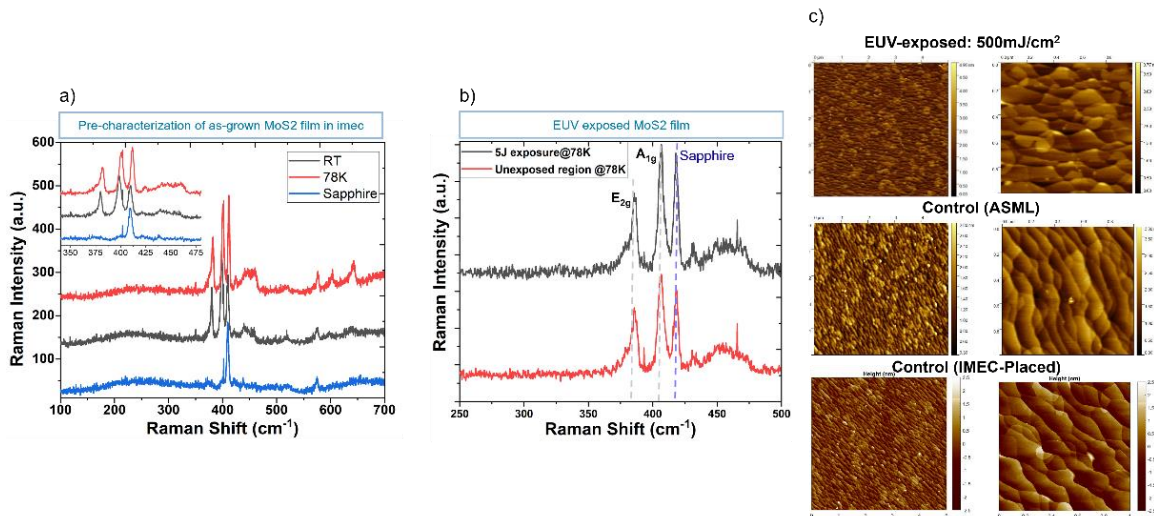


Figure 7 a,b) RAMAN measurements at room temperature and at 78 kelvin before (a) and after (b) EUV exposure to 5 J/cm², c) AFM images of exposed sample to 500 mJ/cm² as well as control samples in two locations.

The superposition of three low temperature photoluminescence measurements in figure 8 shows comparison between non-exposed (blue), exposed to low EUV dose (red) and exposed to high-EUV dose (black) areas of MoS₂ film on Sapphire. I_D is the integral intensity of the defect bound exciton, centered at ~ 1.8 eV, I_A is the integral intensity of the neutral/negative excitons ~ 1.95 eV and I_D/I_A is a measure of defectivity, a qualitative definition for the density of defects on the film. From these measurements, we observe that higher EUV dose, results in generation of more defects. With exposure to lower dose of EUV we have induced ~4.7 times defect compared to the original film and ~12 times more defects via exposure to 5 J/cm². The shift to lower energies (from blue to black peak) can be linked to the creation and accumulation of defects (hence more defects generated at deep energy states).

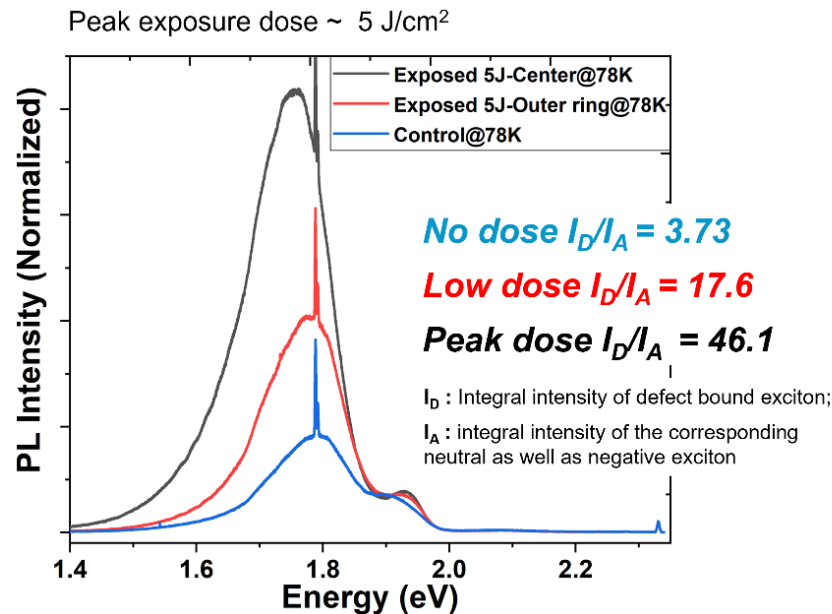


Figure 8 (f) Comparative plot for the low-temperature low-power Photoluminescence characterization of as-grown MoS₂ on sapphire substrate (blue line), exposed to low EUV dose (red line) and high EUV dose (black line). I_D refers to Integral intensity of defect bound exciton; I_A refers integral intensity of the corresponding neutral as well as negative exciton)

This result is an indication of possibility of tailoring 2D films at atomic level with EUV, in order to understand the nature of defects (chalcogen vacancy, oxidation, etc) an elemental surface characterization technique such as scanning tunneling microscope (STM) or x-ray photoelectron spectroscopy (XPS) with a more surface sensitive photon source is required. In a scenario where EUV exposure is followed by exposure to oxygen plasma, missing chalcogens will be replaced by oxygen, which results in doping the layer and hence improving the mobility and performance of the semiconducting MoS₂ film. It is worthy to emphasize that the original defect state of the film, has an impact on further inducing defects on the film e.g. exfoliated single crystals are reported to be more resisting to defect creation while CVD grown films have lower defect creation threshold.

2.2 WSe₂ on Si/SiO₂

We have studied EUV exposure of Intel's WSe₂ crystals grown on Si/SiO₂ by MOCVD. Figure 9 shows the AFM images of the films, where grain sizes of around 1μm cover about 50% of the surface, there are areas of multilayer and bulk like film present as well. The low-temperature photoluminescence measurements on as grown samples show the peak at ~1.6 eV linked to defect bound exciton of WSe₂ [16]. After exposing samples to EUV dose of 300 mJ/cm² and 5J/cm², we observe that the defect peak has shifted towards ~1.37 eV which could be an indication of bulk-like structures [17]. The defect intensity of the higher exposure dose is higher than lower dose. The B_{2g} RAMAN mode observable at 310 cm⁻¹ that only appears in multi-layers and bulk WSe₂ but does not show up in monolayers could be another indication towards a bulk-like sample (figure 11). These are early findings and not leading to a strong conclusion yet, we would like to repeat these experiments on fully closed layers to compare the findings.

Our XPS characterization results on exposed samples hint to increased oxygen content that scales with the EUV dose. Since the substrate (SiO_2) does contain oxygen and it is not fully covered by the WSe_2 layer, we will await results on fully closed layers before concluding that oxidation (doping) is occurring in WSe_2 layer upon EUV exposure [18].

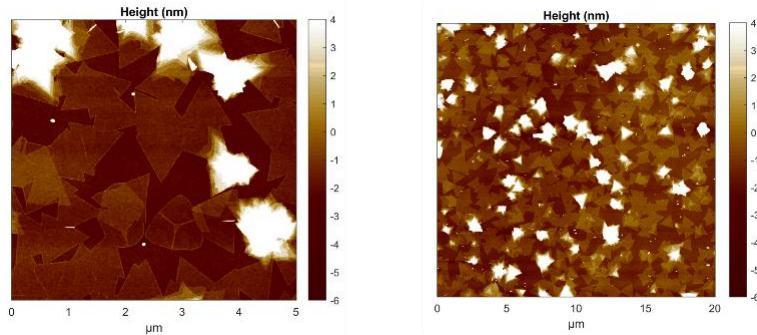


Figure 9 – AFM images of WSe_2 crystals on Si/SiO_2 substrate.

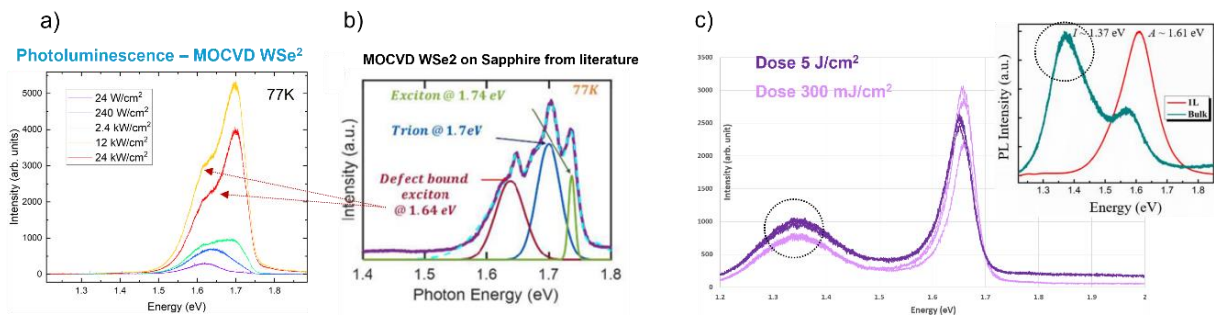


Figure 10 a) PL measurement of as grown WSe_2 film at 77 kelvin with different laser power, the defect bound exciton shoulder appearing at higher powers, b) PL response of MOCVD grown WSe_2 at 77 kelvin from a preprint publication confirming the location of the defect bound exciton at 1.64 eV [16], c) PL response of the EUV exposed WSe_2 film at 80 kelvin with an inset from the supplementary information of the publication [17] confirming the location of the bulk-like peak at 1.37 eV (indirect bandgap emission).

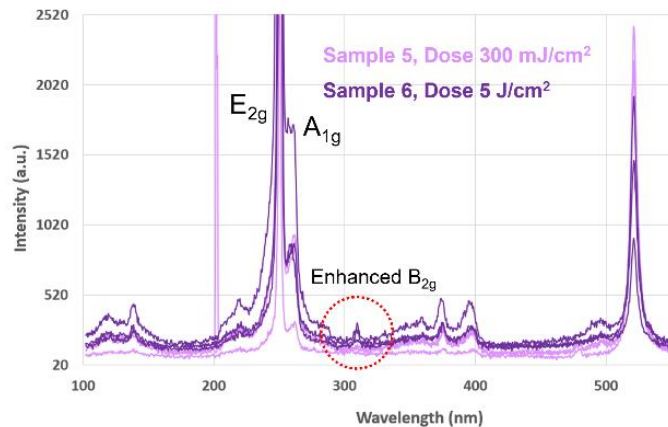


Figure 11- RAMAN response of the WSe_2 film exposed to various doses of EUV, with the enhanced B_{2g} peak as indication for multilayer or bulk-like material [17]

3. CONCLUSIONS AND OUTLOOK

3.1 Conclusions

In conclusion, energetic particles in EUV environment have demonstrated the potential of modifying the properties of 2D layers in vacuum. This is aligned with the published body of research on inducing defects in 2D materials (graphene and TMDs) by irradiation to low energy electron beam, soft-landing ions, plasma environment and a very recent report on capability of patterned EUV exposure in selectively desorbing hydrogen atoms bound to silicon surface [19]. AFM and RAMAN analysis of samples exposed to EUV (in vacuum) do not show sign of structural damage to the film even at high exposure doses of several J/cm². The impact of plasma on these layers is yet to be studied.

Inducing atomic defects with the energy and resolution of EUV enables area-selective processing of 2D layers that can overcome several challenges in extremely scaled devices e.g. local doping for contact resistance improvement, directed etching for resistless patterning or oxidation for improving the TMD performance. During these experiments we noticed that an established growth method with low lot-to-lot variability in crystallin quality is essential for such studies.

3.2 Outlook and next steps

In this report, we have demonstrated setting up a route for studying impact of EUV environment on 2D layers. In order to move closer to the device use case, we will introduce new parameters in the study:

- 1) impact of capping layer e.g. high-k gate dielectric that does protect the surface of 2D layer and at the same time is closer to device structure helps to decouple the environmental impact on the 2D films from the pure impact of EUV photons/electrons (figure 12.a).
- 2) impact of substrate, elements with higher EUV absorption cross-section can generate more secondary electrons
- 3) directly grown vs transferred films, look at the impact on difference in adhesion to the substrate and quality of the film
- 4) study device-like structures (impact on contact resistance, mobility,... before & after EUV exposure)
- 5) demonstration of scaled devices with gate length of 10-14 nm on 300 mm wafer via EUV patterning (figure 12.b and c)

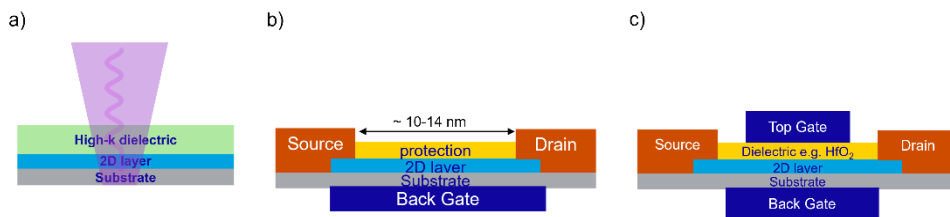


Figure 12 a) schematic of EUV exposure of 2D layer through a capping layer e.g. high-k gate dielectric, b,c) extremely scaled back(and top)-gated planar device with 2D layer as channel, to be build on a 300 mm wafer using EUV patterning

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