Direct Patterning of p-Type Doped Few-layer WSe₂ Nanoelectronic Devices by Oxidation Scanning Probe Lithography

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ABSTRACT

Direct, robust and high resolution patterning methods are needed to downscale the lateral size of 2D materials to observe new properties and to optimize the overall processing of these materials. In this work we report a fabrication process where the initial micro-channel of a few-layer WSe₂ field-effect transistor is treated by oxygen plasma to form a self-limited oxide layer on top of the flake. This thin oxide layer has a double role here. First, it induces the so called p-doping effect in the device. Second, it enables the fabrication of oxide nanoribbons with controlled width and depth by oxidation scanning probe lithography (o-SPL). After the removal of the oxides by deionized H₂O etching, a nanoribbon-based field effect transistor is produced. Oxidation SPL is a direct writing technique that minimizes the use of resists and lithographic steps. We have applied this process to fabricate a 5 nm thick WSe₂ field-effect transistor where the channel consists in an array of 5 parallel 350 nm half-pitch nanoribbons. The electrical measurements show that the device presents an improved conduction level compared to the starting thin layer transistor and a positive threshold voltage shift associated to the p-doping treatment. The method enables to pattern devices with sub-50 nm feature sizes. We have patterned an array of 10 oxide nanowires with 36 nm half-pitch by oxidation SPL.

KEYWORDS: *few-layer tungsten diselenide, scanning probe lithography, nanopatterning, oxygen plasma, p-type doping, transition metal dichalcogenides, nanodevices*

INTRODUCTION

The surface of a few layered transition metal dichalcogenide (TMDC) is highly sensitive to external stimuli of both chemical and physical nature. Conversely, it can be subject to a rich range of chemical¹ and structural^{2,3} engineering strategies to tailor its properties. These features are beneficial to applying doping mechanisms to control the carrier types and performance of the TMDC-based devices⁴⁻⁷ and to use them as ultrasensitive chemical sensors⁸⁻¹⁰ and photodetectors¹¹⁻¹⁴. Consequently, TMDC layers-based electronic devices are being investigated extensively^{15,16}. On the other hand, after the lithography, the removal of resist residues, surface passivation or metal-semiconductor contact improvement must be done using the correct solvent rinsing¹⁷ and plasma exposure^{18,19} for each TMDC compound. To further exploit TMDC materials at the nanoscale a mature development of nanolithographic strategies to fabricate TMDC nanopatterns with feature sizes below or approximate to the quantum and sub-wavelength regimes will give rise to the study of new fundamental phenomena²⁰.

Scanning probe lithography (SPL) is a versatile nanolithographic technique to fabricate high resolution patterns with arbitrary geometries and good overlay accuracy²¹. It has sub-10 nm patterning capabilities^{22,23}; it is performed in ambient conditions, it allows non-destructive, in-situ inspection after fabrication with the same tool. Furthermore, SPL can be used to pattern in a wide variety of materials such as magnetic multilayers²⁴, block copolymers²⁵, self-assembled monolayers^{26,27} or molecular materials²⁸. In particular, oxidation SPL (o-SPL)^{29,30} is a direct, resist-less chemical modification method that has been used to fabricate nanodevices such as III-V semiconductor quantum dots³¹, ballistic transport LAO/STO nanowires³² and silicon nanowire label-free biosensors³³. In the case of 2D materials, the technique has been used extensively to pattern on graphene³⁴⁻³⁷ and also to fabricate nano field-effect transistors (FETs) on MoS₂³⁸, WSe₂³⁹ and black phosphorus⁴⁰ thin layers.

In the present work, we report the application of oxidation scanning probe lithography to fabricate a p-doped, 5 nm thick WSe₂ field-effect transistor with the conduction channel consisting in an array of 5 parallel nanoribbons with 350 nm half-pitch by oxidation scanning probe lithography. The initial few-layer WSe₂ FET prepared by photolithography presents a p-channel conduction. After application of an oxygen plasma treatment, a uniform self-limited oxide layer is formed on top of the whole WSe₂ flake. The presence of this oxide layer on the underlying WSe₂ surface presents two effects. First, there is a p-type doping effect due to the electron transfer at the interface of both materials. And more relevant for our process, the oxide layer screens the crystallographic structure of the dichalcogenide, allowing us to fabricate arrays of oxides with the desired half-pitch and a depth equal to the thickness of the flake by o-SPL. Then, these oxides are removed by deionized H₂O wet etching, generating trenches that isolate electrically the conduction flow through the individual nanoribbons of the final device. Comparing the electrical characteristics between the initial and the final device, it has been shown that the nanoribbons-channel FET conserves the p-doping effect and presents an improved electrical performance with respect to the initial flake wide FET. Additionally, Auger electron spectroscopy measurements were performed on both

the oxide layer formed by the oxygen plasma and the oxides created by o-SPL. The different peak to peak intensities and center shifts show that they are two different type of oxides.

MATERIALS AND METHODS

Oxidation scanning probe lithography

For the o-SPL experiments, WSe₂ (HQ Graphene, Netherlands) thin flakes were transferred onto Au substrates after mechanical exfoliation. These flakes had thicknesses in the 5 – 50 nm range. The results correspond to a sampling of 15 untreated WSe₂ flakes and 15 flakes after oxygen plasma exposure. The size of the sampling and the variety of thicknesses were chosen in order to provide significant data from the o-SPL process to compensate for the tip to tip, substrate to substrate and number of layers variation effects. The width of the patterns is given as full width at half maximum (FWHM).

The oxygen plasma treatment is performed in a low pressure plasma system (Tetra, Diener electronic GmbH, Germany). The sample is exposed for 30 s to the oxygen species generated by applying 200 W (at 40 kHz) in a 0.3 Torr pressure.

The o-SPL process was performed in amplitude modulation⁴¹ mode with a free amplitude in the range of 5 – 10 nm and a set point amplitude/free amplitude ratio in the range of 0.7 – 0.9. We have used a Dimension V AFM microscope, with a Nanoscope V controller (Bruker, USA). An o-SPL oxide is produced by applying a voltage pulse to the sample. The application of the voltage pulse and the tip displacement are controlled by a home-built software. The AFM tips used in the experiments were commercial n⁺-doped silicon cantilevers (NCH-W, NanoWorld, Germany), with a nominal force constant and resonance frequency of about, respectively, 40 N/m and 300 kHz. The oxidation process was performed in a closed chamber to control the relative humidity (RH), in the range of 35% - 55%. The range of applied voltages (V_{ox}) and oxidation times (t_{ox}) is, respectively, 12 V to 30 V and 0.3 ms to 9.6 ms.

Chemical characterization

Auger Electron Spectroscopy (AES) combined with Scanning Electron Microscopy imaging (SEM) has been used to characterize the local chemical composition of the WSe₂ samples upon different oxidation processes. AES spectra were acquired at normal emission in an UHV chamber with a base pressure of 10⁻¹⁰ mbar equipped with a hemispherical electron energy analyzer (SPECS Phoibos 150 spectrometer) and a 2D delay-line detector, using a FEI electron gun as excitation source operated at 25 keV. The low kinetic energy region including C-KLL together with O-KLL, and the high energy Se-LMM and W-MNN Auger transitions were measured using a Fixed Retard Ratio mode of 10 and, an energy step and time/point of 1.0eV and 2s, respectively. Contrary to XPS (X-ray Photoelectron Spectroscopy), AES data are more difficult to quantify in terms of peak areas. Therefore, the as-recorded direct spectra were numerically differentiated to provide the intensity of an Auger transition in a form suitable for quantification in terms of peak-to-peak signals. The AES spectra were analyzed with the CasaXPS program. Data processing for quantitative AES analysis allowed not only the determination of elemental concentration, but also the presence of chemical shifts

associated with the lineshape features in the direct spectra, which are in direct correspondence with the existence of oxidation states in the studied elements.

The diameter of the beam is roughly around 200 nm, while the o-SPL oxidized areas are in the order of 250-400 μm^2 and the studied flakes have areas of around 800 μm^2 , in order to make sure that we were taking the spectra only within each region of interest.

Field-effect-transistor fabrication and electrical characterization

For the fabrication of field-effect transistors, we have used substrates made of 270 nm thermal SiO_2 on Si. The substrates are cleaned by applying three sonication cycles in a solution of $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ (1:1:2) for 10 minutes each and a fourth sonication cycle in deionized water for 5 minutes. The WSe_2 flakes are mechanically exfoliated and transferred onto the SiO_2 substrate by using a commercially available viscoelastic PDMS stamp (Gelfilm, Gel-Pak). Flakes with thicknesses in a range of 5 – 10 nm are selected attending to the color contrast given by optical microscopy. To pattern the source and drain electrodes at the opposite sides of the flake, we have used photolithography followed by electron beam evaporation of 20 nm of Ti and 50 nm of Au. The silicon oxide and the bottom silicon act, respectively, as the gate dielectric and the back gate.

The I-V measurements are performed at room temperature and ambient conditions (RH=30%-40%) in a probe station (Everbeing EB 06, Taiwan) with a semiconductor analyzer (Keithley 4200). The measurements are performed inside a dark and closed chamber to isolate the device from the external light.

RESULTS AND DISCUSSION

Flake surface treatment and o-SPL parameters for patterning nanoribbons

After transferring the mechanically exfoliated WSe_2 thin flakes onto Au substrates, for each used AFM tip, arrays of dots at different relative humidity, applied voltage and pulse time are made to find the oxidation parameters that give the pattern with the best aspect ratio and are useful to fabricate nanoribbons. For all the range of used parameters, 12 V – 30 V of applied voltage, 0.3 ms – 1.8 ms of oxidation time (for a single pulse) and 35% - 55% of relative humidity, the pattern that is created consists in a high circular dot centered in an equilateral triangle with a height between 1 – 2 nm. Fig. 1 (a) shows an AFM topographic image of a line of patterns fabricated at $V_{ox} = 16.2$ V and oxidation times of 0.6, 0.9, 1.2, 1.5 and 1.8 ms (from left to right). The shape of the higher central feature is similar to the oxide patterns that are fabricated by o-SPL in other materials. The triangular component is equivalent to the self-limited oxides with a single-/bilayer thickness that grow preferentially along zigzag edge orientations on WSe_2 flakes that undergo an ozone and thermal treatment⁴². Another expected result is the observed 180° inversion of the oxides triangles in two consecutive layers (Fig. 1(b)) due to the 180° lateral offset between the even and odd number of layers characteristic in TMDC thin films⁴²⁻⁴⁴.

The oxides fabricated by o-SPL grow above and below the material surface. Therefore, the method to measure the total oxide thickness consists in removing the oxide by wet etching. Then, the total oxide thickness is the height of the oxide above the baseline added to the depth of the trench^{45,46}. In the present work, the removal of the oxides was performed by immersion in deionized water for 30 s. The AFM cross section profile of the observed trenches is similar to the one shown in Fig. 1 (e). The depths are only in the range of 1 – 2 nm, independently to the oxidation conditions. Figure 1(f) shows the oxides generated after attempting to pattern an array of nanostripes with a half-pitch of 50 nm. The shape and the pitch of the resulting nanopatterns are far from uniform. In addition, they are very shallow. As consequence these nanopatterns are not suitable to fabricate the dielectric barriers of functional nanodevices.

The above limitation is overcome by treating the WSe₂ surface with oxygen plasma prior to the oxidation SPL step. It has been shown that under oxygen/ozone ambient exposure, the first few-layers of a whole TMDC flake are uniformly oxidized by self-limiting layer-by-layer oxidation^{42,47,48}. The oxygen plasma treatment produces a sub-1 nm thin oxide layer (Figure S1 in SI). By performing o-SPL on the oxide generated by the plasma treatment we are able to suppress the generation of anisotropic structures (triangular-shaped patterns). The oxide dots are isotropic and their growth kinetics follows the well-established features of o-SPL⁴⁹.

Fig. 2(a) shows the AFM topographic image (top) and the corresponding cross section (bottom) of a line of dots fabricated at a fixed $t_{ox} = 2.5$ ms and applied voltages of 24, 25.5, 27, 28.5 and 30 V (from left to right). The heights range from 1.5 nm to 6 nm and the widths, from 27 nm to 59 nm. Fig. 2(b) shows the AFM topographic image (top) and the corresponding cross section (bottom) of a line of dots fabricated at a fixed $V_{ox} = 27$ V and oxidation times of 0.6, 1.2, 2.4, 4.8 and 9.6 ms (from left to right). In this case, the heights range from 1 nm to 7 nm and the widths, from 35 nm to 60 nm. The tip's geometry and sample surface conductivity could change from experiment to experiment. Therefore, the o-SPL parameters V_{ox} , t_{ox} , RH must be optimized for each experiment system. As a guide, the o-SPL parameters V_{ox} , t_{ox} and RH required to pattern few-layer WSe₂ should be above, respectively, 18 V, 0.5 ms and 40%.

The width of the dots shows a quasi-linear dependence. The height of the dots shows a linear dependence with the applied voltage (Fig. 2(d)) and a quasi-logarithmic dependence with the oxidation time (Fig. 2(e)). Each point represented in the graphs shown in Figs. 2(d) and 2(e) is the mean value of an array of 5 dots fabricated with the same tip. The error bars are the corresponding standard deviation. This kinetic behavior is similar to the empirical power-of-time law deduced from the oxidation of silicon by SPL^{49,50}. It can also be observed that the longer the oxidation time, the smaller the vertical growth rate that is represented by the thinner halo-like part of the oxide (Fig. 2(b)). We attribute this effect to the build-up of a space charge characteristic to o-SPL process for long oxidation times⁵¹. The above results predict another common characteristic with o-SPL on silicon. The features with best aspect ratio are the ones using high voltages and short oxidation times⁴⁹.

These WSe₂ local oxides are soluble in water. They are removed after a 30 s immersion in deionized water. The trenches obtained after oxide removal in all the studied samples represented 44% to 46% of the total oxide thickness. This allows us to estimate the depth of the oxide formed below the surface from the height of the oxides above the surface during the SPL step. This is important to fabricate arrays of WSe₂ thin layer nanoribbons for device applications. The oxidation through the whole thickness of the film is necessary to isolate them from the rest of the flake area. A specific example of calibrating the oxidation parameters to fabricate isolated nanoribbons is shown in Fig. 2(c), where the AFM topographic images of the oxide lines after SPL (top) and after DI water etching (bottom) are represented in the top part and the corresponding cross sections are shown superimposed in the bottom part. Three consecutive oxide lines at applied voltages of, from left to right, 25.8, 26.6 and 27.4 V at a $t_{ox}=1$ ms were fabricated on a flake with a thickness of about 8 nm (top topographic AFM image). The heights of these oxides are, respectively, 7, 8.5 and 10 nm (top cross section, black line). After DI water etching, the depths of the trenches are, respectively, 5.6, 7.3 and 8.7 nm (bottom cross section, blue line). It can be observed that only the oxide line fabricated at 27.4 V has penetrated the whole thickness of the flake.

Fig. 2(f) shows the capability of oxidation scanning probe lithography to pattern oxide lines with controlled feature sizes by modulating the oxidation parameters on a WSe₂ surface treated by oxygen plasma. An array of 10 lines with a length of 1 micron and a half-pitch of 36 nm was fabricated by o-SPL using $V_{ox}=18$ V, $t_{ox}=0.5$ ms and RH=49%.

Chemical composition of the oxides by Auger Electron Spectroscopy

Depending on the stoichiometry and the composition of the material to oxidize by SPL, different oxides can be fabricated. As a consequence, the dielectric/conductance properties and the etching selectivity will change depending on the type of oxide. Therefore, spectroscopic measurements are often performed to learn more about the chemical components of the oxides fabricated by o-SPL⁵²⁻⁵⁵. The chosen spectroscopic method depends on the object of study. Spatially resolved photoemission spectroscopy (XPS) on o-SPL patterned MoS₂ thin layers was used to analyze the changes in the electronic structure compared to areas of unmodified surface⁵². Raman spectroscopy was performed to show that it is possible to fabricate MoS₂ monolayers by o-SPL⁵³.

In our work, the main target was to learn if the oxide formed by oxygen plasma and the oxide fabricated by o-SPL were different. To enable the comparison, Auger electron spectroscopy was performed on four different types of sample: a) An untreated WSe₂ surface after mechanical exfoliation, b) a WSe₂ surface after oxygen plasma, c) an untreated WSe₂ surface containing o-SPL oxides in a 400 μm^2 area and d) a WSe₂ surface after oxygen plasma containing o-SPL oxides in a 250 μm^2 area. The differences in the peak-to-peak intensity and the center shifts of the elements Se, W and O with respect to the sample type a) observed from the derived spectra (Fig. 3(a)) served us to interpret the results.

Fig. 3(a) shows AES spectra of the Se-LMM, W-MNN and O-KLL transitions corresponding to the pristine, untreated surface (red curve), the untreated surface with o-SPL oxides (green curve), the WSe₂ surface that underwent an oxygen plasma treatment (blue

curve) and the oxygen plasma treated surface with o-SPL oxides (black curve). The vertical dashed black line constitutes a visual aid to notice chemical shifts compared to the spectra from the unmodified surface. It can be seen that the amount of oxygen on the unmodified WSe₂ surface (red curve) is very low and corresponds probably to a thin native oxide layer, adsorbates from the ambient exposure or both (Fig. 3(b), scheme IV). In comparison, on the o-SPL patterned area of the untreated WSe₂ (green curve), the amount of oxygen has increased considerably, the W peak has shifted towards lower kinetic energy values and the intensity of the Se peak has decreased. This indicates the formation of WO_x on the top of the surface. This oxide screens the signal of the Se from the WSe₂ surface buried by the oxide, which is the reason behind the decrease in the Se peak signal (Fig. 3(b), scheme III).

In the case of the spectrum recorded from the oxygen plasma treated surface (blue curve), several changes are observed. a) The amount of oxygen has increased appreciably. b) A shoulder of higher kinetic energy next to the oxygen peak becomes apparent. c) Both W and Se peaks have shifted towards lower kinetic energy values. d) The intensity of the Se peak is comparable to the W peak. These results show the formation of an oxide rich in both W and Se elements (Fig. 3(b), scheme II). AES spectra were extracted from different points of the whole flake area, obtaining the same result. Therefore, we conclude that a uniform oxide layer is generated after the O₂ plasma treatment. Finally, the spectrum obtained from the o-SPL patterns fabricated on the plasma treated sample (black curve) is very similar to the spectrum obtained from the o-SPL patterns fabricated on an untreated surface (green curve), except for the shoulder present at higher kinetic energy values next to the oxygen peak in the black curve. We interpret this result as the formation of WO_x as the main oxide during the o-SPL process and some minimum amount of residual plasma-formed oxide still present (Fig. 3(b), scheme I).

To summarize this section, the AES spectra taken from o-SPL oxides patterned on a pristine flake and those patterned on a plasma treated flake are almost identical. This indicates that in both cases the patterns (oxides) have identical stoichiometry. The above conclusion is also supported because o-SPL patterns are soluble in water with independence of the surface treatment (see Figs. 1(d), 2(c)). On the other hand, the AES spectrum obtained on a plasma-oxidized flake shows a strong presence of both W- and Se- oxides. We deduce that this oxide is not soluble in water. The height of the plasma exposed surface does not change after immersion in water (see Fig. 2(c)).

p-type doped WSe₂ nanoribbon-based FET: lithography and electrical characterization

A scheme of the fabrication process to get few-layer WSe₂ nanoribbon-based field-effect transistors is shown in Fig. 4(a) – 4(d). A WSe₂ flake is contacted to source and drain electrodes made of a 20 nm Ti/50 nm Au metallic film by using photolithography. This flake also acts a back-gated few-layer WSe₂ field-effect transistor (Fig. 4(a)). The dielectric consists in a 270 nm thick thermal SiO₂ layer. The channel width of this FET coincides with the width of the contacted flake. Then, this FET is treated in oxygen plasma for 30 s (Fig. 4(b)). In the next step, o-SPL is performed to pattern an array of oxide lines with a given periodicity (Fig. 4(c)). The o-SPL parameters are chosen for patterning oxides that penetrate the whole thickness of the flake. This ensures that the conduction path is through the

nanoribbons. Finally, the o-SPL oxides are removed by wet etching in deionized water for 30 s (Fig. 4(d)). This step leaves an array of nanoribbons bridging the source and drain electrodes of the FET.

A nanoribbon-based FET is shown in Fig. 5. It consists in an array of 5 parallel nanoribbons (350 nm wide) on a 5 nm thick WSe₂ flake. The starting width was about 7.7 μ m (narrowest part of the flake, Fig. 5(a)). Each individual trench is produced after H₂O etching of an array of 5 overlapped oxide lines fabricated by o-SPL ($V_{ox} = 22.5 - 27$ V, $t_{ox} = 1 - 2$ ms and RH = 44%). To avoid the current flow outside the conduction path defined by the nanoribbons we have patterned a trench running perpendicular to the nanoribbons (inside the red box marked in Fig. 5(a)). This trench goes from the last nanoribbon to the end of the flake in the opposite side. Fig. 5(b) and 5(c) show, respectively, the AFM topographic image of the nanoribbons and the cross section along the white dashed line marked in 5(b). The protrusions (white mounds) shown in Fig. 5(b) were already present in WSe₂ flake before starting the lithographic processes.

To understand the electrical properties of the nanoribbon-based FET we have measured the I-V output and transfer FET curves through all the lithographic steps depicted in Fig. 4. It is known that WSe₂ FETs range from ambipolar to either predominantly n-channel or p-channel, depending on several factors such as the chosen metal contact⁵⁶ or the concentration of intrinsic defects⁵⁷. The transfer curves of all the devices fabricated and studied in this work have shown a predominantly p-channel behavior, independently of the lithographic step. We have normalized the current by the width of the conduction channel in the curves shown in Fig. 5(d) and Fig. 5(e) in order to separate the channel area reduction effect from the lithography steps. Fig. 5(d) shows the transfer curve of the flake FET before and after oxygen plasma exposure. Before plasma treatment the electrical response shows a p-channel behavior. After oxygen plasma treatment, the transfer curve shows an increase in the current level by three orders of magnitude. In addition, the curve shows a degenerated semiconductor behavior, which is not desirable for electronic applications.

Fig. 5(e) shows the transfer curve of the nanoribbon-based FET. The measurements have been performed approximately 8 hours after the oxygen plasma treatment. The transfer curve shows the features of a non-degenerate p-type semiconductor. This behavior comes from the uptake of adsorbates or organic contamination by the WO_x layer formed after the oxygen plasma treatment. The recovery of the non-degenerated p-type WSe₂ conduction features after exposure to air was observed previously⁵⁸. The threshold voltage has shifted from -6V (flake device) to -2.5 V, which also shows the p-doping effect. These results demonstrate that the nanoribbon-based FET fabrication process by combining oxygen plasma and o-SPL produces devices with better electronic properties than those obtained with untreated flakes.

Our observations regarding the effect of the oxide layer generated by the plasma treatment are consistent with other results. The formation of uniform and self-limited oxide layers on top of WSe₂ has been applied to improve the performance of the devices with respect to those obtained from pristine flakes. A WO₃ layer formed on a few-layer WSe₂ acts as a holes-injector to form Ohmic contacts with Ni¹⁹. A hybrid WO_x/WSe₂ thin film gas sensor

presented larger sensitivity to NO_x at room temperature⁵⁹. Photogating effects⁶⁰ have been observed by forming a WO_x layer on top of a WSe₂ flake.

CONCLUSION

We have developed a direct nano-lithographic process to fabricate p-type doped few-layer WSe₂ nanoribbon-based field-effect transistors. The method combines an oxygen plasma treatment with scanning probe lithography. The first step forms a thin self-limited oxide layer. This oxide layer acts as a hole-dopant for the WSe₂ flake underneath which improves the conduction of the channel. In addition, it contributes to produce a very thin and chemically uniform layer on top of the WSe₂ which facilitates the o-SPL.

We have applied the above process to produce a nanoribbon-based FET consisting in a 5 nm thick WSe₂ FET with an array of 5 parallel 350 nm half-pitch nanoribbons. The transfer characteristics of the nanoribbons FET show a higher current level and a positive threshold voltage shift, characteristic of a p-doping effect with respect to the initial FET after photolithography.

The electron spectroscopy measurements performed by Auger Electron Spectroscopy show differences in the chemical composition of the oxides generated by o-SPL and plasma treatment. The oxides generated by o-SPL are dominated by WO_x species while the plasma treatment shows a significant presence of both W and Se oxides.

The results presented in this work demonstrate that oxidation scanning probe lithography is a direct nano-lithographic technique to fabricate few-layer transition metal dichalcogenide-based nanoelectronic devices under ambient conditions. The method minimizes the use of resists and cleaning steps in the whole fabrication process.

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FIGURES

Fig. 1 o-SPL patterning and kinetics on pristine WSe₂ flakes. (a) AFM topographic image of a line of patterns fabricated at 42% of relative humidity, an applied voltage of 16.2 V and variable pulse times of 0.6, 0.9, 1.2, 1.5 and 1.8 ms (from left to right). Below, the cross section corresponding to the white dashed line is shown. (b) AFM topographic image of o-SPL patterned triangles on two adjacent terraces. The vertical flip shown by the triangles with respect to each terrace reflects the 180° rotation offset between consecutive layers characteristic of TMDC layered materials. The oxidation conditions are V_{ox}=26 V, t_{ox}=1 ms and RH=52%. (c) and (d) show, respectively, the AFM topographic images of the same pattern fabricated at V_{ox}=19 V, t_{ox}=0.6 ms and RH=52%, by o-SPL before and after wet etching in deionized water for 30 seconds. (e) Cross sections along the black and grey dashed lines marked in, respectively, (c) and (d). They are shown overlapped because the oxide grown above the surface and the trench revealed after H₂O etching represent the total thickness of the oxide. (f) Array of lines fabricated at t_{ox}=1 ms, RH=50%, and V_{ox} from 15 to 21 V (from left to right).

Fig. 2 o-SPL patterning and kinetics on WSe₂ flakes treated under oxygen plasma. (a) AFM topographic image of a line of dots fabricated at RH=45%, t_{ox} = 2.5 ms and variable applied voltages of 24, 25.5, 27, 28.5 and 30 V (from left to right). Below, the cross section along the white dashed line is represented. (b) AFM topographic image of a line of dots fabricated at RH=45%, V_{ox} =27 V and variable t_{ox} of 0.6, 1.2, 2.4, 4.8 and 9.6 ms (from left to right). Below, the cross section along the white dashed line is represented. (c) Top panel: AFM topographic image of three oxide lines fabricated by o-SPL at RH=44%, t_{ox} =1 ms and applied voltages of, from left to right, 25.8, 26.6 and 27.4 V. Middle panel: AFM topographic image of the same lines after H₂O etching for 30 s. Bottom panel: The cross sections along the black and blue dashed lines marked in the images above. They are overlapped because the oxide grown above the surface and the trench revealed after H₂O etching represent the total thickness of the oxide. (d) Height of dots as a function of the applied voltage. The RH and the t_{ox} were, respectively, 45% and 2.5 ms. (e) Height of dots as a function of the pulse time. The RH and the V_{ox} were, respectively, 45% and 27 V. (f) AFM topographic image of an array of 10 oxide nanowires with a length of 1 micron and a half-pitch of 36 nm. The o-SPL conditions were V_{ox} =18 V, t_{ox} =0.5 ms and RH=49%.

Fig. 3 (a) AES spectra of the Se-LMM, W-MNN and O-KLL transitions corresponding to the different oxidation processes carried out in this study (left) with the labels where each of the processes is associated with its corresponding curve. As-measured derivative AES spectra were plotted so that evaluation of peak-to-peak intensity provides direct quantification of the contribution of WO_x, SeO_x and their mixture depending of the oxidation process. In addition, the vertical dotted lines denote the energy position of the native oxide. These are used as a reference from which chemical modifications are produced upon o-SPL and O₂ plasma. Readily visual inspection and direct comparison between the samples in each case allow us to emphasize subtle chemical shift differences, and consequently, the formation of WO_x and SeO_x. (b) Schemes of the different interfaces. The sizes and the shapes of the structures are drawn to serve as visual aids.

Fig. 4 Scheme with the fabrication steps of p-type doped few-layer WSe_2 field-effect transistor. (a) Initial few-layer WSe_2 FET. (b) A uniform and ultrathin oxide layer (sub-1 nm) is grown by oxygen plasma treatment. (c) The nanoribbons are fabricated by o-SPL. (d) After the etching in water an array of parallel nanoribbons acts as the conduction channel.

Fig. 5 (a) Optical microscopy image of a finalized device. The white dashed-line area contains the conduction channel of the FET, consisting in an array of 5 parallel nanoribbons. The red dashed-line area contains the trench perpendicular to the nanoribbons fabricated to cut the current flow outside the conduction path. (b) AFM topographic image of the nanoribbons, contained inside the white dashed-line area marked in (a). (c) Cross-section along the white dashed line marked in (b). The nanoribbons have, approximately, a half-pitch of 350 nm. (d) Transfer curves of the device shown in (a)-(c) after different steps during the fabrication process: As a micro-channel WSe₂ thin layer FET after photolithography (black) and after the oxygen plasma treatment, before the o-SPL patterning (blue). (e) Transfer curve after o-SPL fabrication of the nanoribbons and the subsequent wet etching in H₂O.