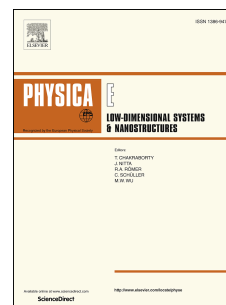


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# Multifunctionalities of 2D MoS<sub>2</sub> self-switching diode as memristor and photodetector

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## Abstract

Self-switching diodes (SSD) were fabricated at the wafer level on a 2D few-layer MoS<sub>2</sub> thin film (7 monolayers) grown on a 4-inch Al<sub>2</sub>O<sub>3</sub>/high-resistivity silicon wafer via Chemical Vapor Deposition (CVD). We report here that MoS<sub>2</sub> behaves as a transparent piezoelectric material in the near infrared spectral region and as a strain-induced ferroelectric material with a measured  $d_{33}$  piezoelectric coefficient of 3-10 pm/V depending on the applied AC voltage. Moreover, we demonstrate experimentally that the SSDs behave as lateral memristors and as photodetectors in the visible spectrum, with responsivities as high as 17 A/W.

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## 1. Introduction

Self-switching diodes (SSDs) are geometrical diodes, which require no doping for rectification [1]. The SSD is in fact a side-gated field-effect transistor [2] that acts as a diode [3], the gates being shorted to the drain. We point out that there are also other types of geometric diodes where the rectification is due only to the shape of a 2D material such as graphene [4].

MoS<sub>2</sub> is the most studied 2D transition-metal dichalcogenide material, which has been used in various applications, such as field-effect transistors [5, 6], microwave switches [7, 8], tunable microwave circuits [9], and energy-harvesting [10]. Recently, we have shown that a 10-monolayer MoS<sub>2</sub> structure fabricated in the shape of a SSD is able to detect microwaves in the 0.9–10 GHz range [11]. Tens of diodes tested for RF detection proved to be square-law detectors and were used to demonstrate a MoS<sub>2</sub> atomically-thin microwave radio [11].

It is known that even the first radio detectors, e.g. galena detectors, were memristors [12]. Galena (PbS) is a semiconductor with the bandgap of 0.4 eV and the first rectifier had a cat-whisker configuration, memristive effects originating from charge trapping mechanisms. In this paper we explore the memristive behavior of the 2D MoS<sub>2</sub> by performing electrical measurements on rectifiers with the same geometry as in Ref. 11. The work reported here shows that MoS<sub>2</sub> SSD diodes can be lateral memristors and photodetectors, functionalities that have not yet been reported.

There are many types of 2D materials working as memristors (see the recent review [13]). The large majority of memristors are two-terminal devices and vertical structures and, where an oxide with a thickness of few nanometers is sandwiched between two metals. These vertical memristors can be integrated in a crossbar array, which is the key circuit configuration for neuromorphic applications, especially in machine learning applications such as pattern recognition [14]. However, vertical memristors suffer from several drawbacks [15], their on-state can be controlled by current compliance, i.e. by limiting the value of the current, but the off-state is far less controllable, requiring a high enough write current to form a stable filament to ensure

stable retention. If these problems are transferred to an array of memristors, they have a direct implication in downscaling and/or selecting the circuits which control the memristors in a cross-bar array.

On the other hand, lateral memristors such as memtransistors a three-terminal device having memristive behavior observable in the drain current-drain voltage dependence at various gate voltages, do not suffer from the above drawbacks, no electroforming is necessary and the current-voltage dependence has a hysteretic behavior that can be tuned by the gate voltage. The first memtransistors were fabricated using MoS<sub>2</sub> grown by CVD, which has a polycrystalline structure, the memristive effects originating from the modulation of the Schottky barrier at the source and drain of the MoS<sub>2</sub> backgate transistor due to migration of sulfur vacancy defects [16]. The 2D MoS<sub>2</sub> in the planar SSD devices presented in this paper are also polycrystalline and lateral memristors, and its memristive properties are due to unique SSD geometry and its physics.

## 2. Fabrication and structural characterization

We briefly explain below the growth of MoS<sub>2</sub> wafer and the fabrication process, which is described in detail in [11]. The MoS<sub>2</sub> that we use here has a nominal thickness of 7 monolayers was grown on a 4-inch 40 nm Al<sub>2</sub>O<sub>3</sub>/HR (high-resistivity) Si wafer and on a c-cut sapphire substrate by Chemical Vapor Deposition (CVD) process at 550 °C using Mo(CO)<sub>6</sub> (99.99% purity) and H<sub>2</sub>S (99.99% purity) as precursors [11]. The TEM image of MoS<sub>2</sub> grown on Al<sub>2</sub>O<sub>3</sub>/HR Si shows that its thickness is 4.5 nm (see Fig. 1(a)). As will be seen further, the thickness of the 2D MoS<sub>2</sub> was also determined from Micro Raman Spectroscopy using a procedure describe by S.-L. Li et al. in Ref. 43 and was found to be 7 monolayers with no observed interfacial oxide. Tens of SSD diodes were fabricated by e-beam patterning and plasma oxygen etching. The diodes were subsequently protected by rectangular areas of HSQ (hydrogen silsesquioxane) patterned by an e-beam lithography process. The channel width of the diodes is 100 nm, the 30 nm Ti/200 nm Au metallic contacts being deposited by e-beam evaporation. The SEM image of the SSD “U-like” unit is displayed in Fig. 1(b). The MoS<sub>2</sub> SSD diode is a periodic

structure consisting of 11 “U-like” units, two consecutive units being separated by 70 nm. The contacts are placed 10  $\mu\text{m}$  above and below the line formed by the “U-like” shapes fabricated in the  $\text{MoS}_2$ .

The atomic smoothness of the  $\text{MoS}_2$  film was confirmed by Atomic Force Microscopy (AFM) with a built-in Piezo-Force Microscopy (PFM) functionality (Tips Nano, CSG01/Pt). The description of the settings used in the AFM and PFM techniques are reported in [17] and therefore will not be repeated here. The tip is placed in contact with the sample and oscillates due to the AC voltage applied between it and the sample. The information is recovered through a lock-in detection scheme at the resonant frequency of the whole tip-sample system.

In Fig. 2(a) we report the topography of the  $\text{MoS}_2$  obtained by scanning a region of 100  $\mu\text{m} \times 100 \mu\text{m}$  in the contact mode. PFM measurements were performed over the same region at 2 different points along a straight line (red circles in Fig. 2(a)), the average roughness and RMS of the sample surface being equal to 0.453 nm and 0.687 nm, respectively. On each point the magnitude and phase of the piezoelectric response were obtained by applying different AC voltages to the tip and a DC bias voltage in the range of  $\pm 10$  V to polarize the sample. The DC voltage is switched off while the tip is moving from one measurement point to the other. We have observed that over those regions on which an AC or DC plus AC voltages are applied through the AFM tip, the surface topography is deformed (see the topography profiles reported in Figs. 2(b,c)) due to the piezoelectric behaviour of  $\text{MoS}_2$  [18].

A more detailed description of the ferroelectric behaviour of  $\text{MoS}_2$  is provided by the analysis of PFM spectroscopy curves for different values of the AC voltage amplitude applied to the tip, as illustrated in Fig. 3. Each plot of amplitude and phase was recorded by scanning the DC voltage between  $-10$  V and  $+10$  V in both directions. Starting from an applied AC voltage with amplitude of around 0.5 V, we observe that both amplitude and phase have a hysteretic behaviour with a phase shift around 200 degrees, indicating the onset of ferroelectricity via strain (see Fig. 3(b)). This finding is in agreement with the fact that strain is a common means to

induce ferroelectricity in many materials, a recently reported example being HfO<sub>2</sub>-based ferroelectrics [19], and is known to induce significant changes in the electronic band structure of MoS<sub>2</sub> [20-22] and even to induce ferromagnetism in MoS<sub>2</sub> with defects [23]. By applying an AC voltage with an amplitude of 0.8-1 V (see Figs. 3(d,e)), the hysteretic dependences are preserved, but the PFM phase shift approaches 360 degrees, indicating that the strain is too high for the onset of ferroelectricity, the polarization states returning to their original orientation.

The strain  $S_j$  developed in a piezoelectric material by the applied electric field  $E_i$  is described by the following matrix equation:  $S_{ij} = d_{ij}E_j$  where  $d_j$  is the piezoelectric coefficient with the unit of m/V. The indices from 1 to 3 indicate components along the  $x$ ,  $y$ , and  $z$  axis of an orthogonal coordinate system. In our case the  $z$  axis is aligned with the direction of the polarization normal to the film plane. The longitudinal piezoelectric constant  $d_{33}$  is evaluated by measuring the displacement  $\Delta z$  of the sample along the applied field  $E_3$ , according to which we can write the linear relation  $\Delta z = d_{33}V$ . Assuming  $E_3 = V/z_0$ , where  $z_0$  is thickness of the sample and  $V$  the voltage applied, the strain along the normal direction can be written as:  $S_3 = \Delta z / z_0 = d_{33}V / z_0$ .

Since  $z_0$  is 4.5 nm, we can estimate for the data reported in Fig.3(d) a normal strain equal to  $S_3 \approx 1.406 \cdot 10^{-3}$  (strain percentage  $\approx 0.14\%$ ), whereas for the data reported in Fig.3(e), in which a different voltage is applied, we get a normal strain equal to  $S_3 \approx 2.197 \cdot 10^{-3}$  (strain percentage  $\approx 0.21\%$ ).

Additional and more quantitative information about the local piezoelectric behaviour of the material can be retrieved from the analysis of the piezo force response, by sweeping the amplitude of the AC voltage from close to zero up to a value beyond the local coercive voltage of the sample. A comparison between the AC-sweep curve and PFM amplitude spectroscopy is reported in Fig. 4(a). By overlapping the AC and DC voltages on the same axis the enhancement of the PFM amplitude is clearly visible in Fig. 4(a) when the AC voltage reaches 0.6-0.7 V, e.g. the value of the coercive voltage, confirming the ferroelectric behaviour of MoS<sub>2</sub> [24, 25]. The

AC-sweep curve is reported in more detail in Fig. 4(b). The piezo-response signal versus the amplitude of the AC voltage applied to the tip shows a quasi-linear dependence (up to a certain value of the voltage). As soon as the amplitude of the AC voltage is higher than the local coercive voltage, the polarization starts to switch with the same frequency as the AC voltage, leading to a strong decrease of the first harmonic response. The piezoelectric constant can be directly calculated from the slope of the linear dependence in the AC voltage [24]. By neglecting the electrostatic force and the tip-indentation effect [25], the values obtained for the piezoelectric coefficients of MoS<sub>2</sub> are ranging from about 3 pm/V to 10 pm/V for a DC voltage between 0 and 1 V. In ferroelectric materials, as soon as the AC amplitude is higher than the local coercive voltage, the polarization starts to switch with the same frequency as the AC voltage, leading to a decrease of the first harmonic response. However, in the range in which the applied AC voltage is around the coercive field, the polarization response of the material is enhanced and it starts being affected by some non-linear behavior, which can be intensified as the DC voltage is increased. This feature could explain the step like behavior reported in Fig. 4 (see ref [26]). The piezoelectric coefficient  $d_{33}$  is 5 pm/V in AlN and 3 pm/V in GaN [27], so that the piezoelectricity of MoS<sub>2</sub> is comparable or even higher than in these two semiconductors used intensively in surface-acoustic wave devices. Other results on MoS<sub>2</sub> indicates piezoelectric coefficient  $d_{33}$  as 3.16 pm/V at 0V and 14.3 pm/V @ 0.1 GPa [28].

Raman spectra were recorded using a Renishaw Invia Reflex micro-Raman spectrometer at room temperature. The Raman mapping was collected on several sites (50  $\mu\text{m}$ ×50  $\mu\text{m}$ , 1  $\mu\text{m}$  step). The samples were excited using a CW Modu-Laser Stellar-REN laser emitting at 514.5 nm with a power of less than 0.4 mW. The reflecting microscope objective was 50X with NA = 0.75 and the excitation spot had a diameter of 1  $\mu\text{m}$ . The back-scattered light was dispersed by a monochromator with a spectral resolution of 1.4  $\text{cm}^{-1}$ , the light being detected by a charge coupled device. The typical accumulation time was 20 s. Raman shifts were calibrated using the



optical phonon frequency ( $520.5\text{ cm}^{-1}$ ) of the silicon monocrystal. Whether the Raman spectrum of bulk  $\text{MoS}_2$  consists of four first-order active modes: at  $32\text{ cm}^{-1}$  ( $E_{2g}^2$ , due to vibration of an S–Mo–S layer against adjacent layers),  $286\text{ cm}^{-1}$  ( $E_g^1$ , which is forbidden in back-scattering on a basal plane),  $383\text{ cm}^{-1}$  ( $E_{2g}^1$ , which is an in-plane mode resulting from opposite vibration of two S atoms with respect to the Mo atom) and  $408\text{ cm}^{-1}$  ( $A_g^1$ , associated with the out-of-plane vibration of S atoms in opposite directions) in [29-33], the asymmetric Raman peak in  $\text{MoS}_2$  multilayers located around  $454\text{ cm}^{-1}$  is associated to a combinational band involving a longitudinal acoustic mode (2LA(M)) and an optical mode ( $A_{2u}$ ) [34].

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Figure 5 illustrates the Micro Raman mapping spectra of 7ML  $\text{MoS}_2$  deposited on the  $\text{Al}_2\text{O}_3/\text{HR Si}$  substrate (left) and characteristic Raman spectrum for 7ML  $\text{MoS}_2$  grown on Si and c-cut sapphire substrates (right). We can observe the presence of two first-order Raman active

modes, at  $383\text{ cm}^{-1}$  ( $E_{2g}^1$ ) and  $408\text{ cm}^{-1}$  ( $A_g^1$ ) [34], the presence of the combinational band in MoS<sub>2</sub> around  $454\text{ cm}^{-1}$  for 2D MoS<sub>2</sub> grown on both silicon and c-cut sapphire substrates and another peak around  $520\text{ cm}^{-1}$  associated to the crystalline Si substrate [35]. For the 2D MoS<sub>2</sub> grown on Si we have employed the calibration procedure for estimating the number of MoS<sub>2</sub> monolayers as proposed by S.-L. Li et al. [35]. The method involved the use of the peak area ratios of MoS<sub>2</sub>  $E_{2g}^1$  phonon mode to Si phonon mode ( $520\text{ cm}^{-1}$ ) and of MoS<sub>2</sub>  $A_g^1$  to Si phonon mode ( $520\text{ cm}^{-1}$ ). The calculated area ratios have been found to be 1.7 and 3.2, respectively, these values corresponding to 7 monolayers of MoS<sub>2</sub> [35]. The observed broadening of both  $E_{2g}^1$  and  $A_g^1$  phonon modes confirms the polycrystalline nature of our 2D MoS<sub>2</sub> thin film and it is consistent with the presence of MoS<sub>2</sub> crystalline domains of about 20 nm.

### 3. Results and discussions

Electrical and optical measurements of SSDs have been performed at room temperature using a calibrated characterization system Keithley 4200 SCS and Agilent Cary 700 UMA spectrophotometer. The DC probes are connected to the Keithley 4200 equipment via low-noise amplifiers and located together with the probe station in a Faraday cage. We have measured all devices at different voltage sweeps, no smoothing software being employed for the experimental data reported here. In total 50 SSDs on the MoS<sub>2</sub> chip were measured and all were shown to exhibit an ambipolar memristive effect, as displayed in Fig. 6. Each  $I$ - $V$  current-voltage dependence from Fig. 6 is formed from 500 current-voltage points which are collected during of 10 s of measurements and followed after 3 s with a new voltage sweep. We observe that the current-voltage dependence is nonlinear above a threshold voltage of about 1 V and presents a pinched hysteretic shape, which shifts to higher currents as the number of sweeps increases.

We distinguish thus the presence of a memory effect, i.e. the current dependence on its former state. All SSDs show the same memristive effect due to the geometry of the device, more precisely due to charging and discharging of surface states on the etched sidewalls of the SSD.

These processes occur at biases that overcome the potential barrier between surface states and the channel [36, 37]. The current-voltage characteristics differ at different sweeps since the initial value of the surface charge modifies after each sweep [37]. So, these slight shifts are due to the potential barrier which is dependent on the number of states. We have observed that memristive behavior is improving increasing the applied DC voltages., but in this case the devices are less reliable i.e. they are destroyed within a day, while applying DC voltages below 5 V produces reproducible results after 1 month. This is due to the fact that we are dealing with very tiny structures with thickness of few nm and thus very high electrical fields are applied on them and degrade their structure.

The time domain measurement of the current at + 5 V, displayed in Fig. 7, shows that the current is progressively increasing as the number of sweeps increases until it saturates and is memorized. By further increasing the number of sweeps, the current does not change, this memory state being changed only by another DC voltage applied on the SSD. This typical memristive behavior has a time constant of tens of seconds, in agreement with results reported in [36]. Similar results are obtained by applying negative DC voltages of, say, -5 V, showing nearly mirror-image curves. Therefore, these measurements are not reproduced here.

The optical transmittance of the MoS<sub>2</sub> film grown on sapphire (samples fabricated in the same run with those grown on 40 nm Al<sub>2</sub>O<sub>3</sub>/HR Si) was measured in the normal incidence configuration using an Agilent Cary 7000 UMS spectrophotometer. Figure 8 shows the optical transmittance of the MoS<sub>2</sub> film grown on sapphire and that of a blank sapphire substrate. We observe that the MoS<sub>2</sub> film has a reasonable good transparency in the visible range of the spectrum (> 50% from 550 nm, and > 75% from 700 nm) and near zero absorption in the NIR spectral range. This finding is in agreement with the low absorption rate of few-layer MoS<sub>2</sub> determined by the indirect bandgap nature of this semiconductor. However, MoS<sub>2</sub> can act as photodetector in the visible and ultraviolet spectral ranges (see, for instance, [38-41]), so we investigated the SSDs response at white light excitation. For this purpose, we illuminated the

SSD with a fiber optic white light source used for the microscope illumination (Motic MLC 150C) of the chuck of the Keithley 4200. The maximum power of this source is 150 W and can be adjusted at different power levels. In Fig. 9 we represented the current-voltage dependence of the SSD at different illuminations, where 100% corresponds to 150 W. We observe that the current is increasing when the power is increased and that the current-voltage dependence is nonlinear and tends to saturate at high optical power.

Assuming that the source has a cross-section with a radius of 5 cm, and that the area of the SSD is about  $190 \mu\text{m}^2$  (see [11]), the responsivity of the device at a bias of 4 V at which the photocurrent is about  $60 \mu\text{A}$  at 100% illumination is estimated at about 17 A/W. The responsivity was calculated as  $R = \Delta I_D / P_{\text{eff}}$ , where  $P_{\text{eff}} = (A_{\text{SSD}} / A_{\text{laser}})P$ , where  $A_{\text{SSD}}$  is the SSD area,  $A_{\text{laser}}$  is the area of white light illumination, and  $\Delta I_D$  is the difference between currents at maximum power  $P$  and under dark conditions. Note that this responsivity is an average value over the white light spectrum, which includes the infrared region in which our few-layer  $\text{MoS}_2$  samples do not absorb, according to Fig. 8. Even so, the obtained  $R$  value is well above the responsivities of previous vertical photodetectors containing few-layer  $\text{MoS}_2$  [39-41], even in those with a bull eye configuration, which reach about 7.3 A/W [36], the explanation of this huge responsivity residing in the horizontal charge carrier transport in SSDs combined with the high quality of the  $\text{MoS}_2/\text{Al}_2\text{O}_3$  interface [42]. It should be mentioned that  $\text{MoS}_2$ -based photodetectors can attain responsivities as high as 880 A/W [43], or even larger, but using monolayer  $\text{MoS}_2$ , which has a direct bandgap and hence a much larger absorption. Also, these photodetectors are made on flakes of  $\text{MoS}_2$  monolayers, while our SSD devices are made at the wafer level. At illumination, the current of the SSD follows the switching on and off of the incident light with time constants of about 1.2 and 0.5 seconds, respectively, as can be seen from Fig. 10; the black vertical lines in the figure are a visual aid for the dependence of the optical power in time, the incident power of the light source varying between 150 W (ON state) and zero/dark condition

(OFF state). The rise time and decay time were obtained from the response of to rectangular excitation by fitting with exponential functions. The rise time and decay time of MoS<sub>2</sub> SSD photodetectors are much lower than those obtained with a MoS<sub>2</sub> monolayer phototransistor [43]. In the case of MoS<sub>2</sub> monolayer phototransistor the rise time is 4s and decay time 9s when on the transistor are applied much higher voltages i.e. a drain voltage of 8V and a gate voltage of -70 V.

#### 4. Conclusions

The work reported here shows that, at the wafer level, few-layer MoS<sub>2</sub> is piezoelectric and can undergo a ferroelectric transition due to electrically induced strain. The ability of 2D MoS<sub>2</sub> to undergo a reversible phase transition is important for many applications, including actuators, surface acoustic-wave devices, and haptic devices in the infrared spectrum where MoS<sub>2</sub> is transparent.

Here we have exploited this reversible phase transition to demonstrate functionalities of both memristors and photodetection in arrays of SSD diode devices. Furthermore, we report that the fabricated SSDs act as excellent photodetectors in the visible spectrum, with responsivity as high as 17 A/W. In conclusion, we have used MoS<sub>2</sub> into novel nano-devices that demonstrate resistive memory capability with potential for neuromorphic device architecture for future telecommunication and computing, as well as very-high-responsivity visible light photodetectors for mobile device applications.

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### Figure captions

Fig. 1 (a) TEM of image of the MoS<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>/HR Si substrate. The MoS<sub>2</sub> thickness is equal to 7 monolayers  $\times 0.65$  nm = 4.5 nm, (b) SEM image of the SSD unit.

Fig. 2 (a) Topography of MoS<sub>2</sub> obtained by AFM, and two profiles acquired (b) along the red dotted line connecting the points of measurements (red circles) and (c) along the direction normal to this line.

Fig. 3 Piezo-Force amplitude and phase curves obtained for the following values of the AC voltage applied to the tip during PFM spectroscopy: (a) 0.1 V, (b) 0.5 V, (c) 0.6 V, (d) 0.8 V, (e) 1 V, and (f) 1.5 V.

Fig. 4 (a) Comparison between the AC-sweep curve and PFM amplitude spectroscopy. The PFM amplitude plots are obtained by sweeping the DC voltage between  $\pm 10$  V and applying to the tip an AC voltage with an amplitude of 0.5 V. Alternatively, the AC-sweep curve is recorded by changing the amplitude of AC voltage in the range between 0.1 V -1.5 V for different DC voltages  $V_{DC1} = 0$  V,  $V_{DC2} = 0.5$  V,  $V_{DC3} = 1$  V. (b) Evaluation of the piezoelectric coefficient of MoS<sub>2</sub> for different applied DC voltages ( $V_{DC1}$ ,  $V_{DC2}$ ,  $V_{DC3}$ ). The coefficients are computed from the slope of the linear dependence in  $V_{AC}$ .

Fig. 5 (a) micro Raman 3D imaging of 7-monolayer MoS<sub>2</sub> deposited on Al<sub>2</sub>O<sub>3</sub>/HR Si substrate (left) (b) the characteristic Raman spectrum 7-monolayer MoS<sub>2</sub> grown on Al<sub>2</sub>O<sub>3</sub>/HR Si and on c-cut sapphire. The phonon mode for the Si substrate is also observed at around 520 cm<sup>-1</sup>.

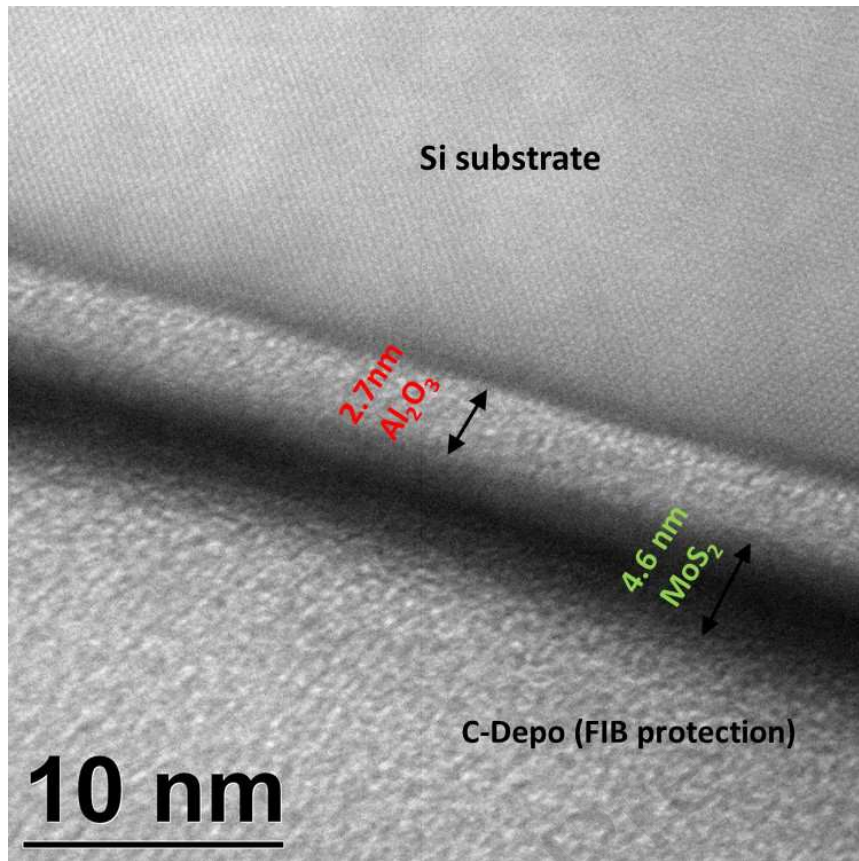
Fig. 6 Current-voltage dependences at various sweeps. Inset: the same curves for both polarities.

Fig. 7 Current-time dependences at various sweeps for a DC voltage of +5 V.

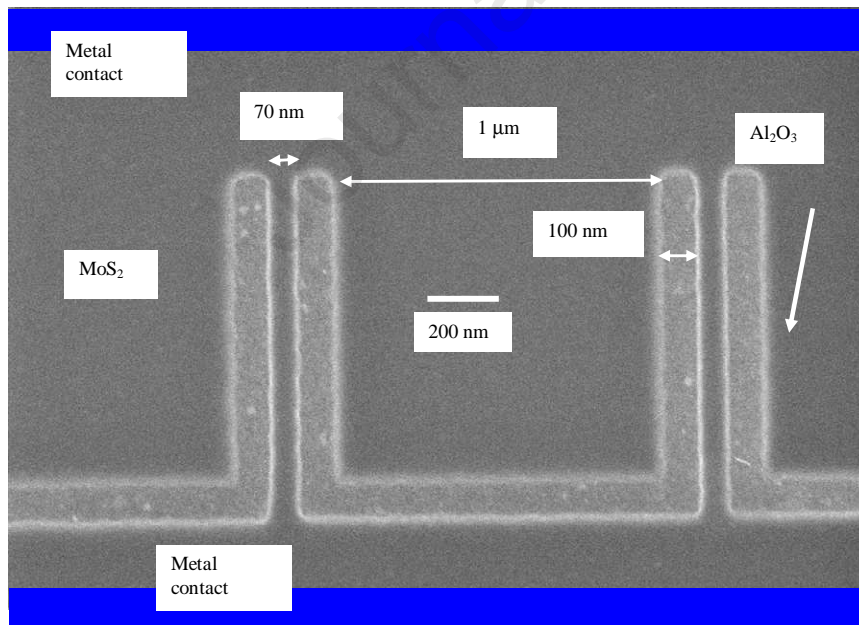
Fig. 8 Optical transmittance of 7-monolayer MoS<sub>2</sub> grown on sapphire substrate and the optical transmittance of a blank sapphire substrate

Fig. 9 Current-voltage dependences at various optical powers indicated as percentages of the maximum power of 150 W.

Fig. 10 Current-time dependence at switching on and off the optical power when the SSD is biased at 4 V.



(a)



(b)

Fig. 1

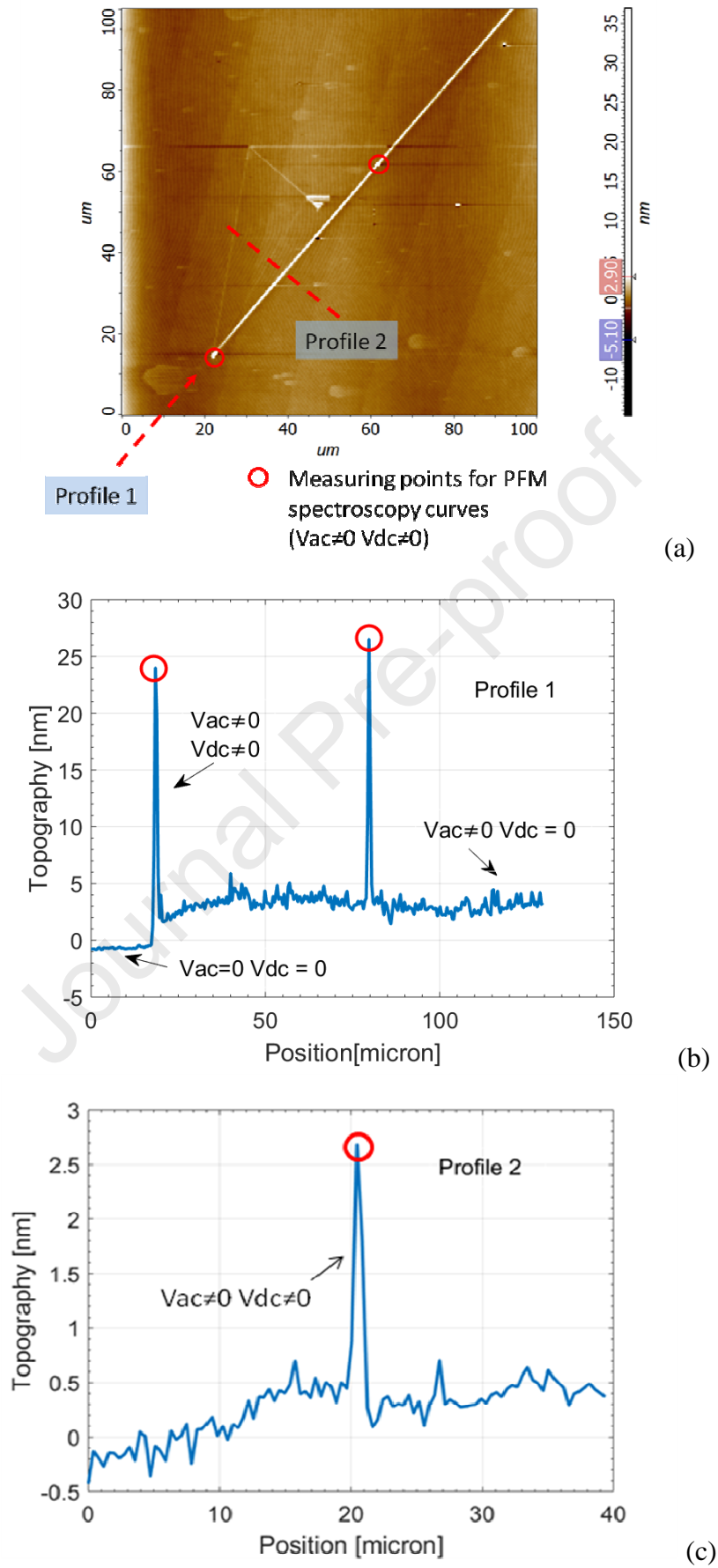


Fig. 2

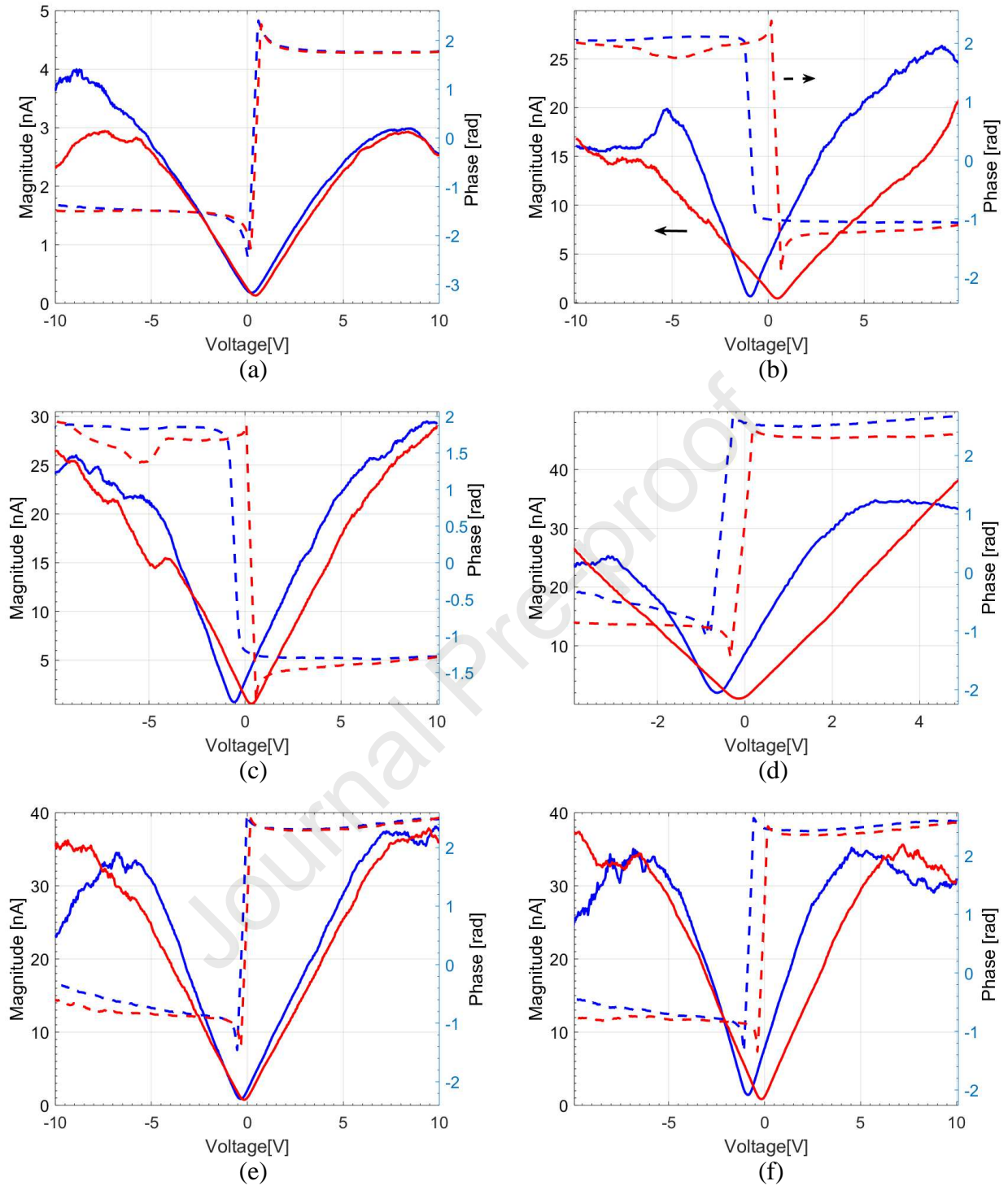


Fig. 3



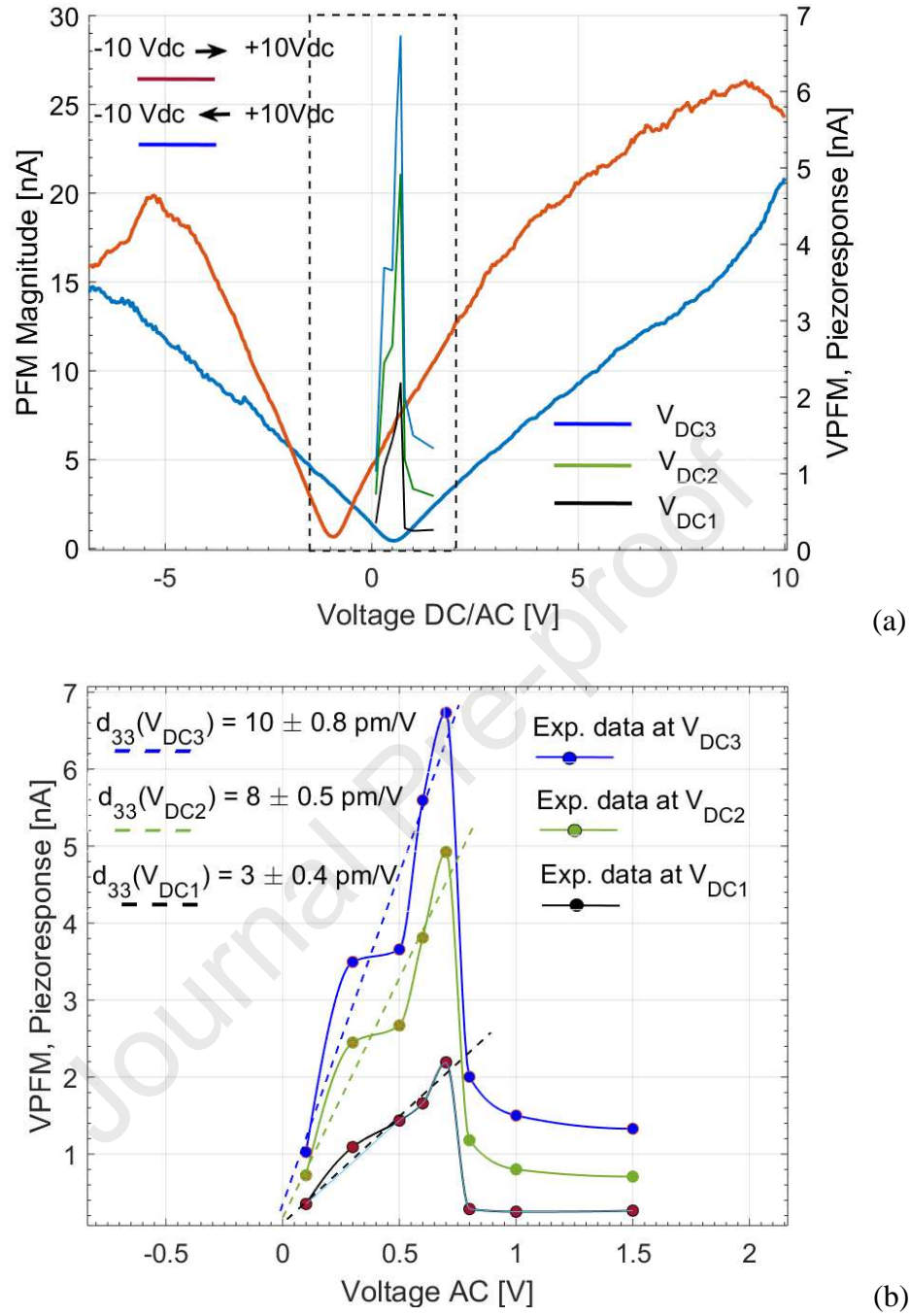
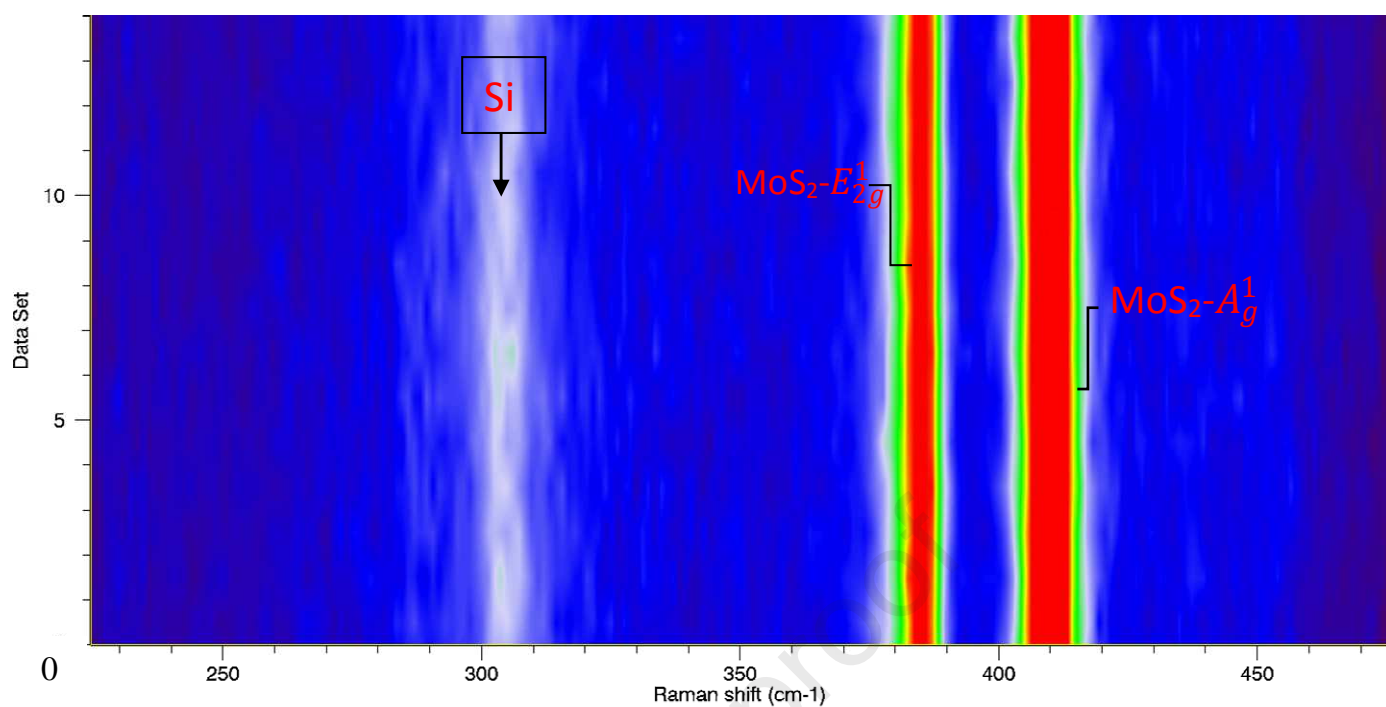
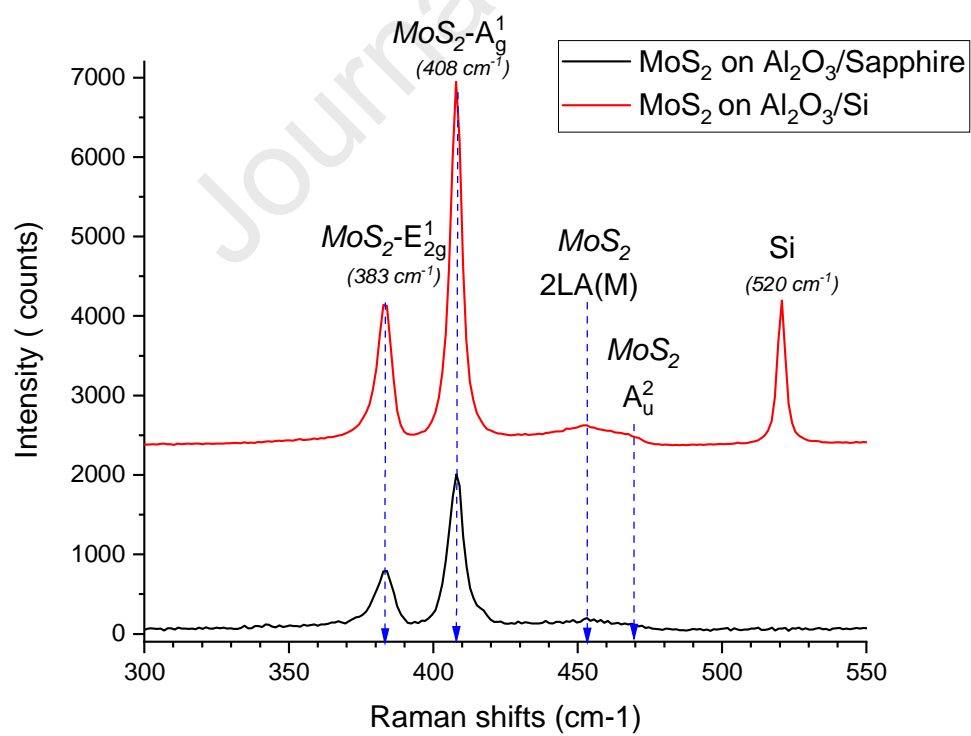


Fig. 4





(a)



(b)

Fig. 5

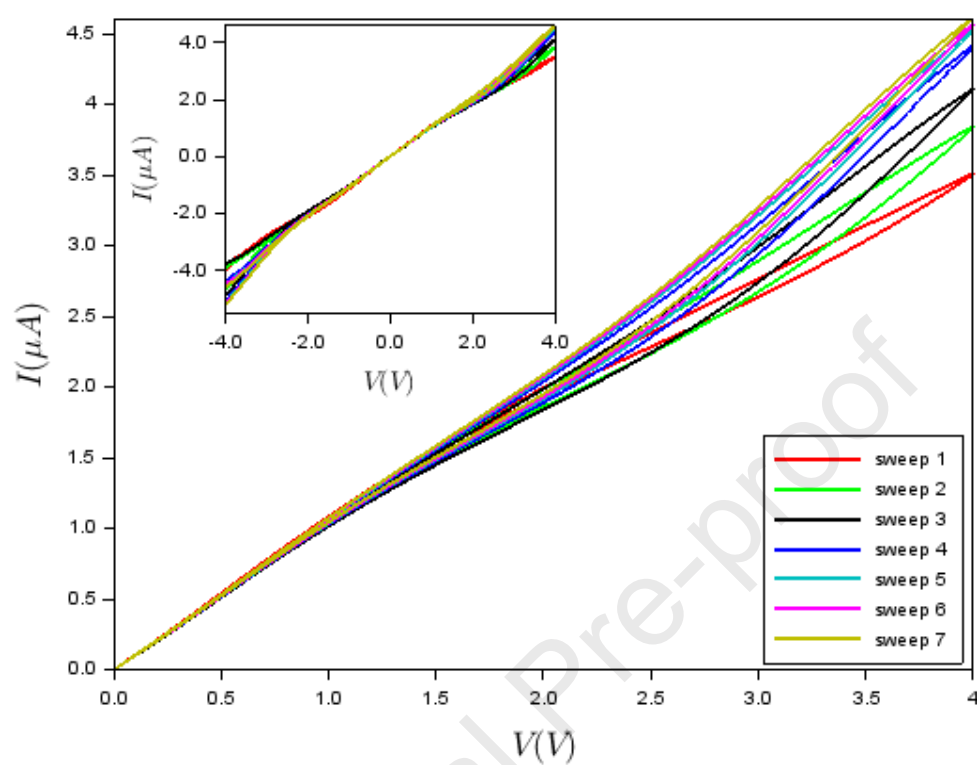


Fig. 6

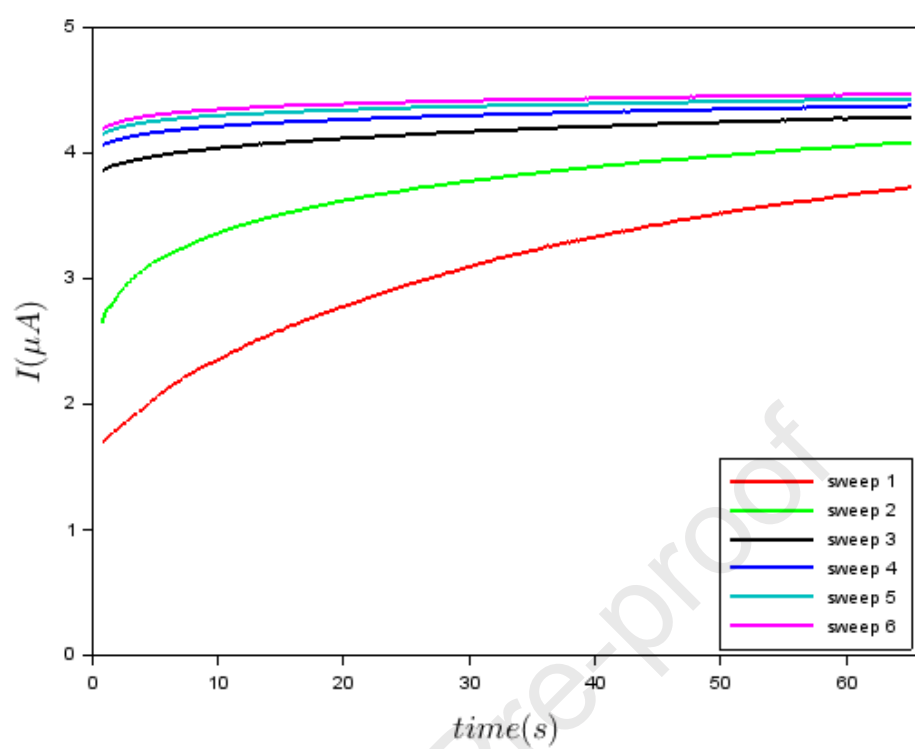


Fig. 7

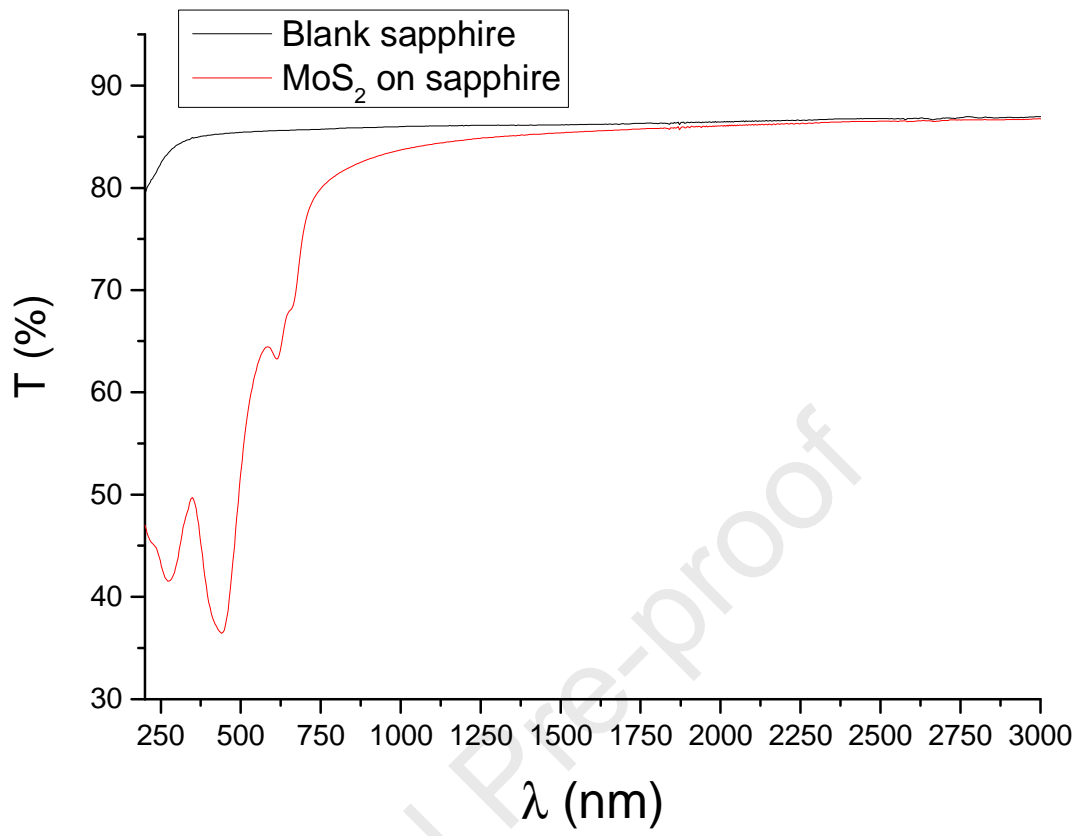


Fig. 8

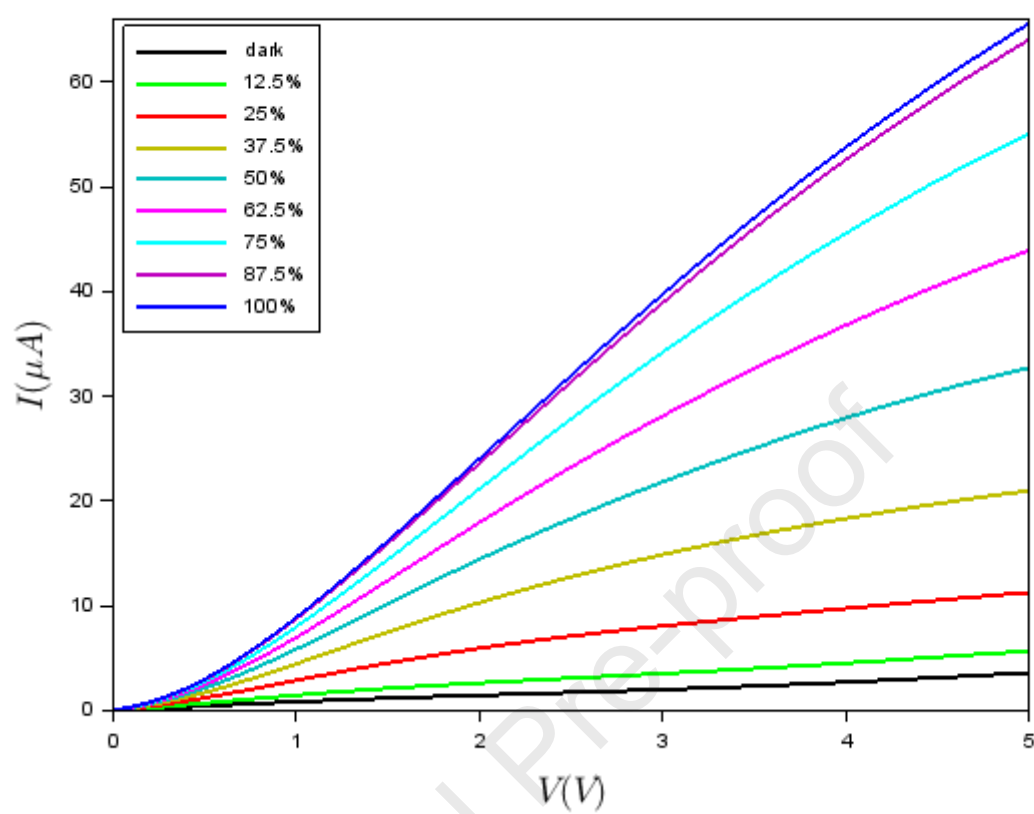


Fig. 9

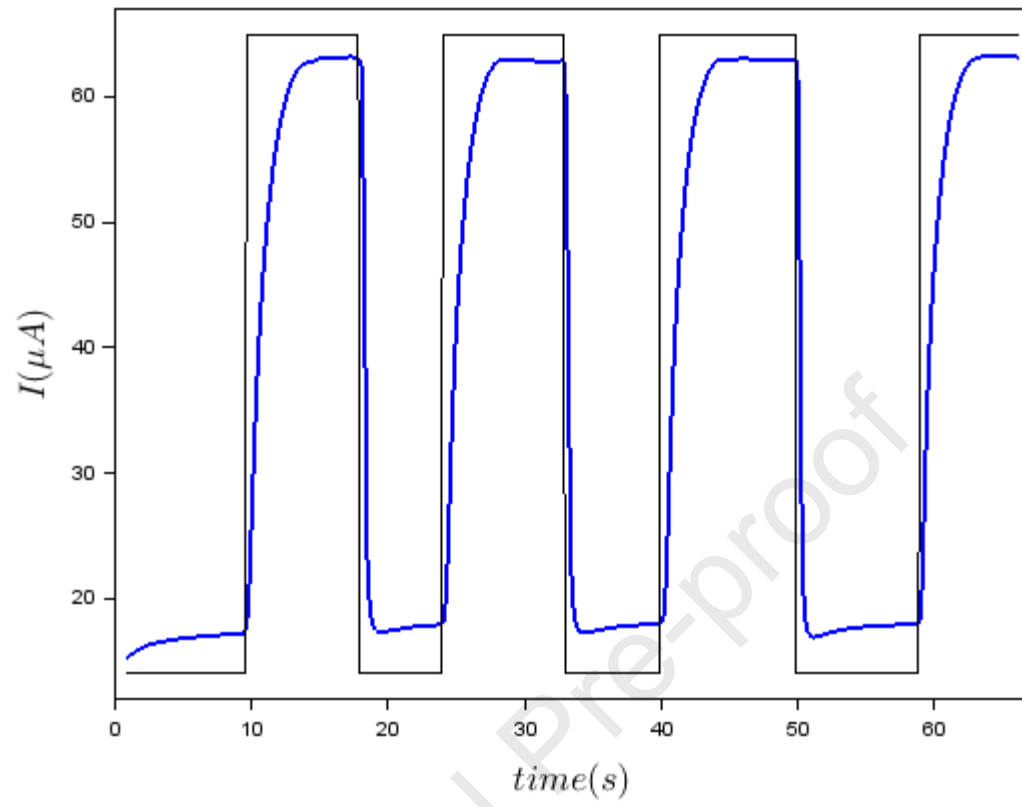


Fig. 10

The authors have contributed equally to this research work.

Journal Pre-proof

**Declaration of interests**

**X** ☐ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: