Femtosecond laser thinning for resistivity control of tungsten ditelluride thin-films synthesized from sol-gel deposited tungsten oxide

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Abstract

In this work we present a route for fabricating WTe$_2$ thin-films together with femtosecond laser post processing, enabling to finely control the conductivity. First, we produce amorphous films of WO$_3$ on Si by spin-casting a sol-gel precursor followed by a consolidating annealing and a reduction process in partial H$_2$ atmosphere, leading to porous metallic tungsten clusters. To achieve WTe$_2$, the samples were exposed to the chalcogen vapours by isothermal closed space vapor transport. The formation of a tungsten ditelluride film composed of piled crystals could be confirmed and a gradient of surface rich Te identified through hard X-ray photoelectron spectroscopy. Finally, it is demonstrated that resistivity can be changed from 0.2 mΩ.m to 1 mΩ.m, while keeping the material characteristics. An anisotropic conductivity can be induced by direct selective thinning with fs laser writing (350 fs pulse duration, 515 nm laser wavelength) of 1D stripes. The obtained results, demonstrate that laser processing is a promising thin-film post-processing technique that can be applied to 2D transition metal dichalcogenides.

Keywords: Transition Metal Dichalcogenides, Tungsten ditelluride, sol-gel deposition, Isothermal closed space vapor transport, fs laser processing.
1 Introduction

Monolayer and few-layered 2D materials are attracting a great attention recently due to their outstanding electronic properties, which give rise to a panorama of new applications in the fields of electronic [1, 2], optical [2, 3], chemical [4-6] and biomedical [7, 8] devices. Among the different families of 2D materials, transition metal dichalcogenides (TMDs) possess unique properties and have applications in various fields such as gas sensing, photocatalysis and energy storage devices [9-11]. TMDs have the form MX$_2$, where M is a transition metal and X is a chalcogen (S, Se, or Te) bound by strong covalent bonds in a 2D plane and forming layers bound by weak Van der Waals forces out of that plane. The versatility of properties of TMDs is partly due to their polymorphism, where metal coordination changes from distorted octahedral to trigonal [12]. For example, the well-studied MoS$_2$ is a semiconductor in its trigonal prismatic (2H) phase, which is the stable phase at room temperature. But when it shows up to the metastable octahedral (Td) phase, it presents a semi-metallic behaviour [13].

WTe$_2$ is one of the 2D materials belonging to the transition metal dichalcogenides family [14]. At ambient conditions, WTe$_2$ usually presents an orthorhombic (Td) phase [15]. This Td phase behaves as a semimetal [16] and has been found recently to have extremely high and no saturating magnetoresistance [17], as well as pressure-induced superconductivity [18]. Meanwhile, WTe$_2$ in its metastable trigonal prismatic (2H) phase is a semiconductor, and due to its bandgap and effective mass, is viewed as an integral part of the tunnel field effect transistor (TFET) [19].

One of the methods for obtaining large area few monolayer TMDs is the annealing of the transition metal (or the transition metal oxide) in the presence of vapours of a chalcogen element. So, sulfurization [20], selenization [21] and tellurization [22] have been frequently employed to prepare the corresponding TMDs.
While WS\textsubscript{2} [23] and WSe\textsubscript{2} [24] have been obtained by this method, there are only a few reports of successful tellurization of tungsten [25, 26].

In this paper, we report the preparation of WTe\textsubscript{2} by tellurization of previously deposited tungsten oxide films grown by sol-gel. We performed isothermal close space (ICS) Tellurization in a small volume and a semi-closed graphite crucible. In such a configuration, the Te vapor pressure approximately equals its equilibrium vapor pressure at the temperature of the annealing, and the Te source/substrate distance is very small. These characteristics favour the Te vapor transport and the efficiency of the tellurization [22, 25].

Additionally, we present results on selectively controlling the resistivity of the WTe\textsubscript{2} thin film after femtosecond laser irradiation. Femtosecond laser processing of thin films has been applied to a wide variety of materials, such as the technologically important silicon-on-insulator [27] or indium-tin oxide [28]. In most cases, micrometric modifications are achieved by generating laser-induced periodic surface structures (LIPSS), which offers the advantage of enabling rapid patterning through self-organization processes without the need for intense focusing conditions. However, direct laser writing, despite being a slower processing strategy, is generally preferred for triggering modification by strongly focusing the beam, thereby avoiding structuring through material self-organization. This strategy has been demonstrated to have strong potential for laser thinning of TMDs via precise control of their thickness (down to single layer) [29]. Here, we show the possibility to precisely thin WTe\textsubscript{2} via laser direct writing with femtosecond laser pulses (350-fs pulse duration and 515-nm wavelength). The control on the laser parameters, as the micrometric control on the line-to-line separation or the fluence of irradiation, enables to tune the resistivity and induce
electrical anisotropy, without inducing chemical or thermal-related changes on the thin-film.

2 Experimental Methods

2.1 Tungsten oxide film preparation

The WO$_3$ precursor sol was prepared using tungsten (IV) chloride powder 95% metal basis (Sigma Aldrich). A 0.8 M solution was prepared with the tungsten powder in ethanol. On the other hand, a solution of ethanol, hydrochloric acid and water was prepared in a 0.001:1:0.005 volume ratio, respectively. Both were left to rest for 30 minutes. Then, they were mixed to obtain a final solution with a concentration of 0.39 M, like that of previous studies with TiO$_2$ [30] and MoO$_3$ [22].

A precursor droplet of 50 $\mu$L was deposited onto (100) Si surface while spinning at 2000 rpm. The condensed films obtained were then annealed in open air for 10 minutes at three different temperatures. The whole spin-casting/annealing process was repeated 3 times to produce thicker films. This first step is illustrated in the left part of figure 1.a.

2.2 W and WTe$_2$ film preparation

The nucleated structures produced by sol-gel spin-coating were subsequently reduced at atmospheric pressure in H$_2$:Ar at 1:5 atmosphere at 600ºC for 1h, which eventually allowed achieving W films.

For the isothermal closed space vapor (ICSV) tellurization, a graphite boat with a Te solid precursor was used. The sample annealed at 600 ºC with a reducing gas mixture composed of H$_2$:Ar at 2:3 was exposed to the Te source for 15 minutes at atmospheric pressure [31]. The ICSV process is illustrated in the right part of figure 1.a.
2.3 Film thinning by direct laser writing.

The laser processing of the thin-films was carried out using a Satsuma HP2 Yb fiber laser from Amplitude Systems. The fundamental wavelength of the laser is 1030 nm with a pulse duration of 350 fs and emitting with a tuneable repetition rate between 1–500 kHz. Additionally, through a modulus for generating harmonics, 515 nm radiation is accessible. Since the motivation of this work is to produce precise direct laser modification, the smaller spot size provided by this shorter wavelength motivates its use.

The laser power is attenuated with filters and fine controlled by the software of the laser system. The beam is focused to the sample by making use of a microscope objective (x20 NA 0.4), as sketched in Figure 1 (b), having a Gaussian spot size diameter at the sample position of 3.1 μm (1/e²). The sample is mounted on a motorized XYZ-axis platform (Aerotech) and perfectly aligned perpendicular to the laser beam. By moving the horizontal axis (X-axis) at a controlled speed of 10 mm/s and by setting the...
repetition rate at 50 kHz continuous and homogeneous modified lines are inscribed on the material. The laser peak fluence range is tested in processing the samples, finding that the optimum peak fluence to produce controlled thinning is between 85 mJ/cm$^2$ and 170 mJ/cm$^2$. As a reference, under the same irradiation conditions amorphous lines in silicon were produced by using fluence values of 120 mJ/cm$^2$. Areas of 3.5 x 3.0 mm$^2$ are processed by writing horizontal lines and controlling the vertical line-to-line separation, exploring in this work separations of 2 and 4 µm. To illustrate the speed of the process the machining time is 15 min. for the vertical separation of 2 µm and 7 min. and 30 s for the separation of 4 µm.

2.4 Characterization.

A morphological analysis was performed using a Field Emission Scanning Electron Microscope (FESEM) FEI VERIOS 4i and X-ray diffraction (XRD) with a Panalytical diffractometer X’Pert PRO (θ/2θ geometry, Cu anode and non-monochromatic (K$_\alpha$) radiation). The synchrotron X-ray diffraction experiments were performed at BM25-B SpLine at the ESRF providing a wavelength of 0.8434 Å in a six-circle diffractometer in vertical geometry [32]. Raman spectra were obtained with a Renishaw Ramanscope 2000 spectrometer and an Argon ion laser emitting at a wavelength of 514.5 nm. The laser power was maintained low to avoid sample damage. A metallographic optical microscope Olympus BH-2 was used to focus the laser light on the film and to collect the light scattered by the sample in a backscattering geometry. The optical axis was perpendicular to the sample surface. Hard x-ray photoelectron spectroscopy measurements were performed at the BM-25 SpLine beamline of The European Synchrotron, Grenoble, France [33]. The experimental set-up includes a high electron kinetic energy analyser working from a few eV up to 15 keV [34]. All data were analysed using CasaXPS software after subtraction of a Shirley baseline,
correcting charge shifts and determining chemical contribution through Gaussian/Lorentzian peak fitting. To measure the IV curve, four gold contacts have been circumscribed in the circular area of the sample and arranged in a gridded cross. The distance between the points of the cross is 2 mm so that they remain inside the irradiated area. A four-point station with millimetric control of electrical contact positioning was used to interconnect with the IV acquisition system (Bio-Logic).

3 Results and Discussion

The first step was to analyse the growth process of the thin film. For this we characterized the nucleation of the sol-gel tungsten oxide film by means of SEM. Figure 2 (a, b) shows the SEM images of the tungsten oxide samples. With an annealing temperature of 600ºC we obtained a very porous, thin film resembling a gelly-paste. A cross section image (not shown) demonstrated a uniform thickness of 270 nm after only one spin-coating droplet. This thickness was increased by repeating the process. At 800ºC, the condensed film transforms. The formation of clusters, with a variety of geometric shapes and smooth edges is observed. Also, the size range is quite wide, from 100 to than 300 nm. The appearance of these clusters is a phenomenon widely observed in WO₃ deposition processes involving a liquid phase precursor, such as in sol-gel [35].

Then we studied the transformation induced by the annealing of the spin casted film and its reduction process by X-ray diffraction. Figure 2 (c) shows the diffractogram of the samples after the first condensation annealing of the scheme of figure 1 (a). The phase that best corresponds to the experimental data, for both temperatures, is the monoclinic, γWO₃ (P 1 21 /n 1, COD 2106382) with unit cell parameters a=7.306 Å, b=7.504 Å and c=7.692 Å, which corresponds to the most stable WO₃ phase [35, 36]. All the peaks have been identified with this phase except the one that appears at 2θ≈38º,
which is due to the substrate [22]. The raise of the (020) peak at $2\theta\approx23.51^\circ$ after annealing at 800°C may be related to the previously described clusterization change observed by SEM, implying a growth of three-dimensional structures. A worsening of the signal to noise ratio and decrease in sample intensity (note relative increase of substrate related peak), is also observed in the sample treated at 800°C. This is again related to the formation of WO$_3$ clusters, leading to a non-conformal film compatible with a visible substrate, as observed by SEM in figure 2.b.

In figure 2 (d) the X-ray diffractograms of the samples reduced by annealing in the presence of H$_2$ are shown. The peaks correspond to metallic W in its two crystalline phases: the metastable $\beta$-W (Pm -3 n, COD 9008583) [36-38] and the stable W-bcc (Im - 3 m, COD 9011611) [36]. Both are cubic with lattice parameter $a=5.083$ Å and $a=3.158$ Å, respectively. If the structure of $\beta$-W is a modification of the metallic tungsten or rather a suboxide, has been debated for a long time, but it seems more likely that it is a true modification of metallic tungsten [36]. The composition of the sample reduced at 600°C obtained by Rietveld refinement was 56% $\beta$-W phase and 44% bcc W. Meanwhile, in the sample treated at 800°C only W-bcc phase is present. Although it is not the main objective of this work, an additional method of growth for the two tungsten phases is presented. The synthesis of both W bcc as of $\beta$-W may be relevant for microelectronic and spintronic applications, respectively [37].
Once the reduced samples were analysed, the one synthesized at 600°C was selected for the conversion to WTe$_2$ by means of isothermal closed space tellurization. We chose the 600°C annealed sample because it is formed by a more continuous sheet and not by clusters as grown at 800°C (see figure 2 a-b). After the tellurization, a significant change is observed in the morphology. The film changes from porous to a compact nanobricks film, as shown in figure 3 (a-b). Also, the thickness of the tellurized samples increase, reaching 300 nm, due to the incorporation of Te in the structure, which increases the specific volume of the material [25].
WTe₂ exists in two crystalline phases with very different properties. The 2H (P6₃/mmc) structure has semiconductor properties, while the Td (Pmn2₁) is a semimetal [25, 39]. In the diffractogram of figure 3 (c) both structures are compared with the one obtained experimentally. As can be seen, there is a contribution from both structures. However, also diffraction peaks that correspond to hexagonal Te (COD 1011098) are
present. Contrary to similar previous studies, there is no preferential growth of the WTe$_2$ in the [001] direction [25]. Making use of Rietveld analysis the sample is composed of 75% WTe$_2$ (of which 90% is present in the 2H structure), and 25% Te with a 5% of calculated error. This Te excess is produced during cooling post-tellurization [40]. It is important to highlight that this Te excess is not seen in SEM images and has very high crystal quality, so it must be present in the form of inlaying crystals within the WTe$_2$ nanobricks. The Raman spectrum, figure 3 (d), confirms the presence of WTe$_2$ and Te. The A$_{17}$ and A$_{19}$ modes have been named according to the notation in the literature [25, 41]. There is no peak at 272 cm$^{-1}$, which corresponds to the monoclinic WO$_3$ [40], which indicates that all the tungsten in the films is tellurized.

HAXPES measurements were performed to characterize sample’s composition in depth and determine if the tellurization process is superficial or proceeds smoothly to the substrate interface. Figure 4 (a) shows the HAXPES spectrum for the W 3d core level. Using three different X-ray energies we can study the chemical changes of this element that occur deeper in the film. The binding energy has been calibrated with the Si 1s peak at 1840 eV [42]. It is obtained that the highest intensity peaks have a binding energy (BE) of 2.7 eV above the BE of W 3d core level for the pure metal [43]. Several studies show that a BE displacement of less than 1 eV is expected for the W 3d core level of the W-Te bond [44, 45]. Therefore, by comparison it can be deduced that the peaks obtained at 1783 and 1845 eV (figure 4) correspond to the 3d$_{5/2}$ y 3d$_{3/2}$ core levels of WTe$_2$, respectively. The smaller peaks at 1823 and 1885 eV are due to a non-stoichiometric oxide since they are at a higher BE [44, 45]. In figure 4 (b) the relative area attributed to each bonding has been extracted. This value is related to the amount of the said bonding in the sample. The intensity of the Si 1s increases as the energy of the photons does. The higher the energy of the X-ray beam, the higher the energy of the
ejected electrons and therefore photoelectrons from deeper parts of substrate are detected. On the other hand, the relative area of the peaks attributed to WTe$_2$ decrease with increasing energy, while those related to WO$_x$ increase. These facts indicate that the tellurization occurs in depth and not only on the surface of the thin film. The fact that there is a higher proportion of WTe$_2$ on the surface than in the bulk suggests that a diffusion process proceeds consistently. Thus, the thin film grown is not uniform in-depth and although the main component is the WTe$_2$, some WTe$_{2}$O$_{1-x}$ can be predicted in depth thanks to the HAXPES study.

Figure 4. (a) W 3d and Si 1s core level spectra acquired at three different X-ray energies (7.5; 9 and 10.5 keV) where two main W 3d contributions (WTe$_2$ and WO$_x$) can be distinguished. (b) Quantitative comparison of the concentration of WTe$_2$ and WO$_x$ as a function of the x-ray energy determined using the 3d$_{5/2}$ component.

With the aim of controlling the resistivity and inducing electrical anisotropy in the thin film, inscription of horizontal lines with selective line-to-line separation has been made by direct laser writing. In particular, large areas have been fabricated by using the following combinations: line spacing of 2 μm and peak fluence of 170 mJ/cm$^2$, spacing of 2 μm and peak fluence of 85 mJ/cm$^2$ and spacing of 4 μm and peak
fluence of 170 mJ/cm². Under the conditions of this later case, figure 5 (a) shows the characteristics of the surface of the WTe₂ thin-film after laser processing, demonstrating the high spatial resolution of the laser inscription since the lines are clearly not overlapping. This is also confirmed for spacing of 2 μm, as observed in the cross-section image in Figure 5 (b), were the modified regions are clearly separated by pristine areas. Additionally, this image also shows that for the higher fluence used (170 mJ/cm²) the thin film is not fully ablated, and the written channels have approximately 1 μm width. Images in figure 5 (c-d) show the composition map obtained by EDX before and after laser irradiation. In figure 5 (d) is observed that in the regions modified by laser irradiation there is a decrease of W as well as of Te. Therefore, it can be indirectly deduced that the laser only generates thinning, since the signal of both compounds does not completely disappear. Additionally, we can also deduce that oxidation is not produced, since the signal of Te does not decrease significantly with respect to the one of W, as expected in case of oxidation.

Figure 5. (a) SEM micrograph of a selectively laser thinned region with 4-μm line separation with a peak fluence of 170 mJ/cm². (b) SEM image of a cleaved sample of a
selectively laser thinned region with 2-µm line separation with a peak fluence of 170 mJ/cm². (c-d) Composition maps obtained by EDX for W and Te: (c) the as grown thin-film and (d) after thinning by laser irradiation with 4 µm line separation at a peak fluence of 170 mJ/cm².

Placing four cross-shaped electrical gold contacts the electrical resistivity has been measured in a perpendicular and parallel direction to the lines generated by laser writing. No metal-semiconductor junction behavior has been observed in the IV curves. This is important because it allows confirming that no oxidation of WTe₂ is induced; since WO₃ is a semiconductor and WTe₂ is mostly identified in the 2H semiconductor phase in our films [46]. This reinforces the hypothesis that selective laser thinning does not induce total ablation, nor drastic oxidation, supporting the above mentioned EDX concentration maps. The resistivity values obtained from the experiment are shown in Figure 6 and are in agreement with the expected laser thinning effect. An increase of the resistivity is observed with respect to the as-synthesized material. The resistivity values obtained are within the order of magnitude for Td-WTe₂ in bulk form [14], which suggests a dominant electrical transport effect of this phase in spite of being the minor phase according to Rietveld refinement. Regarding these results, there are two main observations of applicative interest: a) a notorious resistance anisotropy and b), the possibility to finely tune resistivity values. The observed resistance anisotropy is originated by the geometry of the laser irradiation induced modifications. The conductivity in an axis perpendicular to the line direction is decreased since electrons find periodic abrupt changes on the thickness along its propagation. A quantitative analysis of this induced anisotropy indicates resistivity values larger for the perpendicular direction with respect the parallel one, reaching a factor close to 2 for all
the tested irradiation conditions. Regarding the tuning of resistivity values, this is achieved by either the laser fluence or by the line-to-line separation. First, varying the laser fluence, which enables to control the quantity of removed material, demonstrates that higher the fluence (170 mJ/cm²) higher the increase of resistivity. Secondly, the same logic applies when comparing surface processed with less or more line separation. As the density of lines decreases (greater separation) the change is less significant because the total surface modified is smaller.

Figure 6. Comparison of the resistivity between the perpendicular and parallel directions, with respect the direct laser writing conditions: line spacing and laser peak fluence. The rest of the direct laser writing parameters are kept the same: sample speed of 10 mm/s and laser repetition rate of 50 kHz.

These results confirm the advantages of laser thinning over other techniques such as mechanical exfoliation. There is a great precision in the control of the amount of material that is removed (control of the final thickness), which is crucial for the properties of two-dimensional materials. In addition, with this technique a spatial
control of the slackening process is achieved, which allows the generation of structures with great precision or, as in this case, inducing anisotropy.

4 Conclusions

This work introduces a synthesis route composed to obtain thin films of WTe$_2$. First, using the sol-gel technique, a condensation annealing and a heat treatment in a partial H$_2$ atmosphere, the precursor W sheets are obtained. With the subsequent isothermal closed space tellurization of these sheets, it is possible to obtain 300 nm sheets of WTe$_2$ with a microstructure of nanobricks. The presence of WTe$_2$ is confirmed by X-ray diffraction and Raman spectroscopy. An in-depth study of the resulting film after tellurization with hard X-ray photoelectron spectroscopy confirms that the 300 nm is mainly composed of WTe$_2$, with an increasing WO$_x$ content at the interface with the substrate.

In addition, by selective and precise thinning by femtosecond direct laser writing, it has been demonstrated the final tuning of the resistivity of WTe$_2$ as well as the possibility to easily induce electrical anisotropies. These anisotropies are conceived as potential sources for gas sensing.

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