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XPS study of the thermal vapour sulfurization of tungsten thin films

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ABSTRACT

Here we report the XPS spectra of thermally sulfurized tungsten thin films on SiO_2 at different temperatures. The sulfurization was performed in a chemical vapour deposition system at 400 ºC, 500 ºC, 550 ºC, 600 ºC and 750 ºC. Below 500 ºC XPS showed that the tungsten layer was oxidized (W^{6+}) and only carbon-sulfur compounds were detected. On the other hand, from 600 ºC the sulfurization process was complete by forming WS_2, while at the intermediate temperature of 550 ºC the films were partially oxidized and partially sulfurized.

1. INTRODUCTION

Transition metal dichalcogenides (TMDs) are quite promising 2D materials due to their amazing properties [1-4]. They follow the general form of MX_2 in which M and X are transition metal and chalcogen atoms, respectively. Among others transition metals, molybdenum and tungsten are the most used, producing MoS_2 and WS_2 when sulfurized, respectively. Nowadays, these materials are subject of intense research around the world due to the broad range of their possible applications [5]. Thus, several applications in fields such as nanoelectronics [1], optoelectronics [6], spintronics [6] and energy conversion [7,8], among others, have been proposed. Nevertheless, the development of low-cost techniques for synthesising thin films of TMDs for the above-mentioned applications remains an ongoing challenge.

The most used methods for the synthesis of TMDs are liquid exfoliation [9] and chemical vapour deposition (CVD) [9,10], which usually produce inhomogeneous samples. On the other hand, thermal vapour sulfurization (TVS) [11,12] seems to be better positioned for growing large-area high-quality TMDs. It consists in a two-step process in which a transition metal is firstly deposited on a substrate and then sulfurized in a CVD system [11,13,14]. Nowadays, there is a huge research on both the method for pre-depositing the metal on a substrate as well as the conditions for its sulfurization [11]. In fact, metal deposition have been carried out by following different chemical and physical methods, such as drop coating, atomic layer deposition, sputtering, pulsed laser deposition and thermal evaporation [14].

In this work, we characterized by X-ray photoelectron spectroscopy (XPS) the TVS of tungsten layers at different temperatures to obtain WS_2. Tungsten was deposited on SiO_2 by thermal evaporation from a filament under vacuum conditions. This report shows that W remains oxidized when the TVS is carried out at temperatures lower than 500 ºC. On the other hand, for temperatures higher than 600 ºC the TVS process is complete, forming WS_2 on SiO_2.

2. METHODS

SiO_2 substrates were cleaned with acetone and ethanol in an ultra-sonic system.

A tungsten wire with a diameter of 0.25 mm was used for W thermal deposition on SiO_2 at an electrical current of 10 A under a pressure of $5x10^{-3}$ mbar.

The sulfurization was carried out in a CVD system, where sulfur powder was heated at 170 ºC while the sample temperature was ramped at 10 ºC/min until reaching the target value. A combination of N_2 (4 l/h) and H_2 (1 l/h) was used during TVS at a pressure of 10 mbar.

XPS spectra were acquired in an Ultra High Vacuum (UHV) system with a base pressure of $2x10^{-10}$ mbar. The system is equipped with a hemispherical electron energy analyzer (SPECS Phoibos 150), a delay-line detector and a monochromatic AlKα (1486.74 eV) X-ray source. High-resolution spectra were recorded at normal emission take-off angle and with a pass-energy of 20 eV, which provides an overall instrumental peak broadening of 0.5 eV.

3. RESULTS

First, a desired quantity of tungsten was deposited on SiO_2 by thermal evaporation under vacuum conditions. This evaporation was performed by flowing an electric current through a tungsten filament. Then, the samples were introduced in a CVD system for their sulfurization following an optimized procedure described in [11]. Roughly, the samples were introduced at the heating zone of a CVD system while an alumina boat containing S was located at the entrance of the quartz tube and independently heated.

Figure 1 shows a scheme of a tungsten thin film growth and its subsequent thermal vapour sulfurization.

The TVS of tungsten layers was followed by XPS. This technique allows to detect the elements at the sample and their chemical environment. Figure 2 shows the XPS results obtained after TVS at 400 ºC, 500 ºC, 550 ºC, 600 ºC and 750 ºC. Figure 2a, 2b and 2c show the W 4f, S 2p and O 1s XPS regions, respectively. Moreover, W $5p_{3/2}$ appears at higher binding energies (BE) of Figure 2a.

Two different regimes were identified by XPS, below 500 ºC (black and red spectra in Fig. 2) and above 600 ºC (blue and violet spectra in Fig. 2). Moreover, at an intermediate temperature of 550 ºC (green spectra in Fig. 2) the shape of W 4f, S 2p and O 1s XPS spectra can be described as the convolution of the low and high temperature spectra (see below).

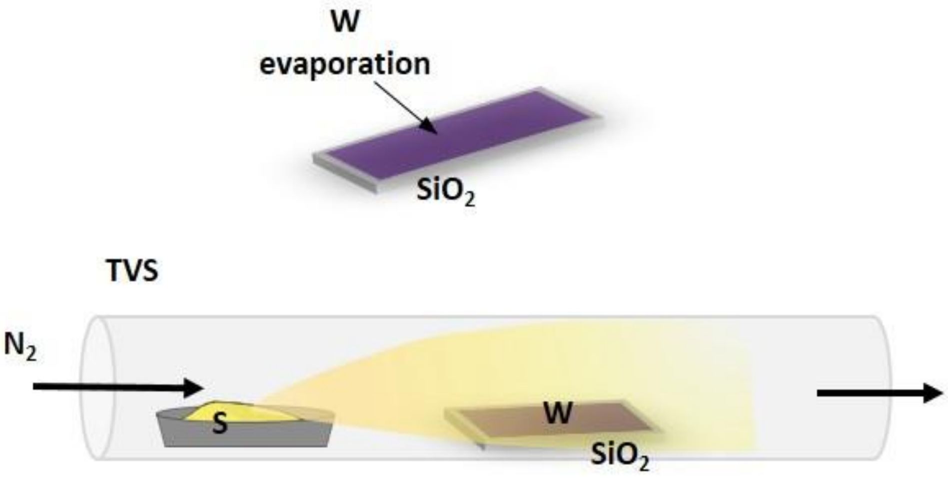

Figure 1. Scheme of the protocol used for growing WS_2 thin films. A pre-deposited W film on SiO_2 was thermally vapour sulfurized.

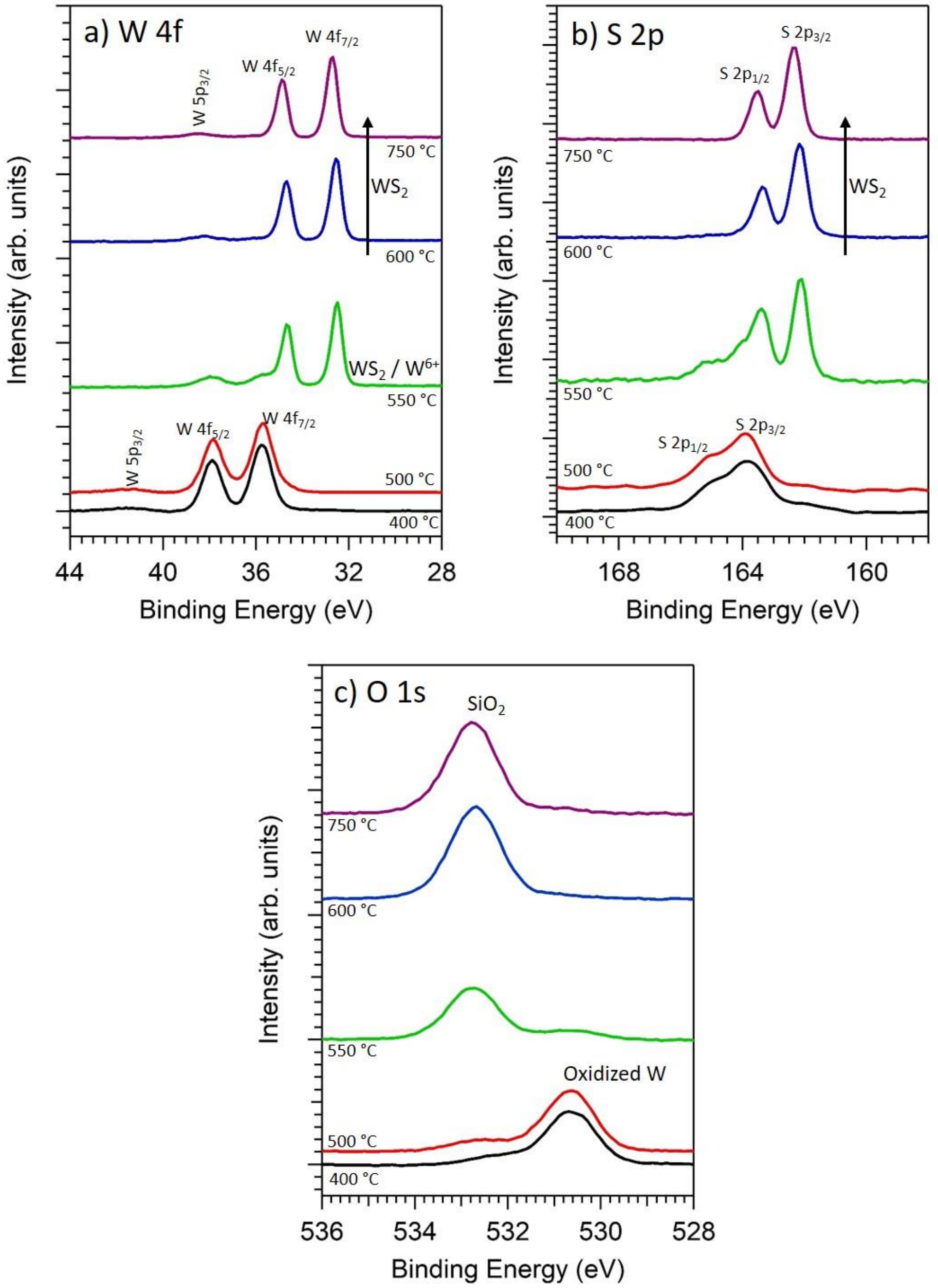

Figure 2. XPS normalized spectra of the tungsten thin film after thermal vapour sulfurization at

400 ºC (black spectra), 500 ºC (red), 550 ºC (green) and 600 ºC (blue) and 750ºC (violet). a) W 4f, b) S 2p and c) O 1s regions.

Below 500 ºC, W 4f had two main XPS peaks centred at BEs of about 35.8 eV and 37.9 eV, ascribed to W $4f_{7/2}$ and W $4f_{5/2}$, respectively. These BEs were in good agreement with previous reported values for oxidized tungsten *i.e.* W^{6+} [15-18]. On the other hand, in the low temperature regime, S 2p showed two broad peaks centred at BEs of about 163.9 eV and 165.1 eV corresponding with S $2p_{3/2}$ and S $2p_{1/2}$, respectively. These BEs are higher than the expected values for S atoms in a WS_2 chemical environment (blue spectra of Fig. 2b). On the contrary, XPS indicated that at the low temperature regime, some sulphur atoms were deposited on oxidized tungsten film but not forming

WS_2. In fact, these BE values are compatible with C-S species, suggesting the presence of some organo-sulfur compounds [19]. Importantly, the S/W ratio obtained by XPS at the low temperature regime was 0.58, significantly lower than that expected for WS_2. Moreover, two peaks appeared in the O 1s region at BEs of about 532.8 eV and 530.7 eV. The peak at higher BE was ascribed to the oxygen atoms of the SiO_2 [20] substrate while the second peak corresponded with WO_3 [17,18].

A completely different scenario was obtained by XPS at temperatures higher than 600 ºC in which both W 4f and S 2p strongly shifted to lower BEs. W 4f had two main peaks centred at BEs of about 32.6 eV (W $4f_{7/2}$) and 34.7 eV (W $4f_{5/2}$), values which were in good agreement with previous reported BEs for W atoms in a WS_2 chemical environment [15,16,21]. Moreover, the extra peak centred at a BE of 38.3 eV was ascribed to W $5p_{3/2}$ from WS_2 samples [15,16,22]. Complementary, S 2p presented two sharp peaks at BEs of 162.2 eV (S $2p_{3/2}$) and 163.4 eV (S $2p_{1/2}$) as it was expected for sulfur atoms in WS_2 samples [15,16,21,22]. Thus, XPS indicated that WO_3 transformed into WS_2 after TVS at temperatures higher than 600 ºC. Accordingly, the peak ascribed to WO_3 in the O 1s XPS region vanished in the high temperature regime (see Fig. 2c).

4. CONCLUSIONS

XPS analysis of the thermal vapour sulfurization of oxidized tungsten thin films on SiO_2 showed that the reaction started at temperatures higher than 500 ºC, although the complete transformation to WS_2 was obtained from 600 ºC. Thus, at the intermediate temperature of 550 ºC, the films were partially oxidized and partially sulfurized. In XPS spectra of WS_2 films obtained from 600 ºC W $4f_{7/2}$ was centred at a BE of around 32.6 eV while S $2p_{3/2}$ appeared at 162.2 eV.

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REFERENCES

[1] S. Manzeli, D. Ovchinnikov, D. Pasquier, O. V. Yazyev and A. Kis, *Nat. Rev. Mater.* **2**, 17033 (2017).
[2] G.H. Han, D.L. Duong, D.H. Keum, S.J. Yun and Y.H. Lee, *Chem. Rev.* **118**, 6297 (2018).
[3] W. Choi, N. Choudhary, G.H. Han, J. Park, D. Akinwande and Y.H. Lee, *Mater. Today.* **20**, 116 (2017).
[4] X. Duan, C. Wang, A. Pan, R. Yu and X. Duan, *Chem. Soc. Rev.* **44**, 8859 (2015).
[5] S.A. Han, R. Bhatia and S-W. Kim, *Nano Converg.* **2**, 17 (2015).
[6] V. Sorkin, H. Pan, H. Shi, S. Y. Quek and Y.W. Zhang, *Crit. Rev. Solid State Mater. Sci.* **39**, 319 (2014).
[7] H. Li, X. Jia, Q. Zhang and X. Wang, *Chem.* **4**, 1510 (2018).
[8] X. Yu and K. Sivula, *ACS Energy Lett.* **1**, 315(2016).
[9] H. Wang, C. Li, P. Fang, Z. Zhang and J. Z. Zhang, *Chem. Soc. Rev.* **47**, 6101 (2018).
[10] D. K. Sharma, E. V. Ramana, S. Fateixa, M. J. Hortigüela, G. Otero-Irurueta, H. I. S. Nogueira and A. Kholkin, *Mater. Res. Bull.* **97**, 265 (2018).
[11] M. J. Hortigüela, I. Bdikin and G. Otero-Irurueta, *Thin Solid Films* **691**, 137588 (2019).
[12] I. Hotovy, L. Spiess, M. Sojkova, I. Kostic, M. Mikolasek, M. Predanocy, H. Romanus, M. Hulman and V. Rehacek, *Appl. Surf. Sci.* **461**, 133 (2018).
[13] C-R. Wu, X-R. Chang, C-H. Wu and S-Y. Lin, *Sci. Rep.* **7**, 42146 (2017).
[14] H. F. Liu, S. L. Wong and D. Z. Chi, *Chem. Vap. Depos.* **21**, 241 (2015).
[15] L. Wu, A. J. F. van Hoof, N. Y. Dzade, L. Gao, M. I. Richard, H. Friedrich, N. H. De Leeuw, E. J. M. Hensen and J. P. Hofmann, *Phys. Chem. Chem. Phys.* **21**, 6071 (2019).
[16] F. Perrozzi, S. M. Emamjomeh, V. Paolucci, G. Taglieri, L. Ottaviano and C. Cantalini, *Sensors Actuators B Chem.* **243**, 812 (2017).
[17] R. Ji, D. Zheng, C. Zhou, J. Cheng, J. Yu and L. Li, *Materials* **10**, 820 (2017).
[18] S. Li, Z. Yao, J. Zhou, R. Zhang and H. Shen, *Mater. Lett.* **195**, 213 (2017).
[19] T. Liu, Z-W. Cui, J. Zhou, Y. Wang, Z-g. Zou, *Nanoscale Res. Lett.* **12**, 375 (2017).
[20] T. V. Larina, L. S. Dovlitova, V. V. Kaichev, V. V. Malakhov, T.S. Glazneva, E. A. Paukshtis and B. S. Bal'zhinimaev, *RSC Adv.* **5**, 79898 (2015).
[21] D. Escalera-López, R. Griffin, M. Isaacs, K. Wilson, R. E. Palmer and N. V. Rees, *Appl. Mater. Today* **11**, 70 (2018).
[22] A. P. Shpak, A. M. Korduban, L. M. Kulikov, T. V. Kryshchuk, N. B. Konig and V. O. Kandyba, *J. Electron Spectros. Relat. Phenomena.* **181**, 234 (2010).