SYNTHESIS OF MoS$_2$ BY TREATING MOLYBDENUM IN H$_2$S PLASMA

SINTEZA MoS2 Z OBDELAVO MOLIBDENA V PLAZMI H2S

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MoO$_3$ samples were sulfurized in a radiofrequency plasma created in H$_2$S gas. The power was set to 800 W (H-mode) to achieve sufficient sample heating and thus MoS$_2$ formation. The treatment time was varied between 2 s and 30 min. The samples were analysed by X-ray photoelectron spectroscopy (XPS). The results showed MoS$_2$ formation already at short treatment times (2 s). With increasing treatment time, the sulphur concentration decreased and became negligible at 90 s of treatment. XPS-depth profiling showed the formation of a 5-nm-thick MoS$_2$ layer on the sample treated for 2 s.

Keywords: molybdenum sulphide, H$_2$S plasma, sulfurization, XPS

Vzorce MoO$_3$ smo sulfurizirali v radiofrekvenčni plazmi, ustvarjeni v plinu H$_2$S. Moč generatorja je bila 800 W (H-način razelektritve), s čimer smo dosegli zadostno gretje vzorcev in s tem tvorbo MoS$_2$. Čas obdelave smo spreminjali med 2 s in 30 min. Vzorce smo analizirali z rentgensko fotoelektronsko spektroskopijo (XPS). Ugotovili smo, da se MoS$_2$ tvori že pri kratkih časih obdelave (2 s). S podaljševanjem časa obdelave je koncentracija žvepla upadala in pri 90 s obdelavi postala zanemarljiva. Pri profilni globinski analizi XPS smo na vzorcu, obdelanem 2 s, ugotovili nastanek 5 nm debele plasti MoS$_2$.

Ključne besede: molibdenov sulfid, plazma H$_2$S, sulfurizacija, XPS

1 INTRODUCTION

MoS$_2$ is an important compound belonging to transition-metal dichalcogenides. It is a layered 2D material with properties similar to graphene.[1] The advantage of MoS$_2$ over graphene is its thickness-dependent electrical and optical properties.[2–4] Therefore, it is a promising material for applications in photonics and photovoltaics (solar cells),[5–7] the microelectronic industry (integrated circuits,[8] tunnelling transistors,[9] flexible electronic devices[10]) and for energy conversion (fuel cells,[11] batteries[12]). MoS$_2$ is usually formed by chemical vapour deposition (CVD) using MoO$_3$ and sulphur[1] or by annealing of thin evaporated molybdenum thin film in a sulphur-containing environment.[2] In both cases, high-temperature is required. Najmaei et al. synthesized MoS$_2$ by CVD at 850 °C.[1] A. Tarasov et al.[2] was heating the samples at 550–1050 °C for 1 h. He found that the structural quality (stoichiometry) of MoS$_2$ was greatly improved at higher temperatures (above 750 °C). Weber et al.[13] was heating MoO$_3$ samples in a H$_2$S atmosphere for 3 h in the temperature range up to 400 °C. The fully sulphated state of Mo appeared at temperatures between 250 °C and 400 °C. X. L. Li et al.[14] was heating MoO$_3$ and sulphur in a furnace up to 850 °C.[14] Pure hexagonal MoS$_2$ was formed at temperatures above 400 °C; however, the best temperature was found to be 850 °C. At temperatures below 400 °C sulfurization was not complete because MoO$_3$ oxide was still found to coexist.

When they were investigating the effect of treatment time, they found that a short treatment time led to the coexistence of an intermediate product of MoO$_2$ and MoS$_2$, no matter at what temperature the reaction was performed.[14]

Another possibility for the synthesis of MoS$_2$ is plasma-assisted sulfurization of MoO$_3$.[15,16] The advantage of using plasma is the presence of atomic and ionic species of hydrogen and sulphur, which are more reactive than H$_2$S itself. Kumar et al. used H$_2$S/Ar plasma for the synthesis of MoS$_2$ films at different temperatures (150–550 °C) for 1 h.[15] He found similar results as Li et al. Above 350 °C the films were predominantly MoS$_2$, whereas below 350 °C two phases existed: MoS$_2$ and MoO$_2$. Therefore, a two-step mechanism of sulfurization was suggested: the first one involving the reduction of MoO$_3$ to MoO$_2$, followed by the second one involving the replacement of oxygen with sulphur in MoO$_2$ to form MoS$_2$.[15] It was also found that the size of the MoS$_2$ crystallites was increasing with the temperature. In another experiment, P. Kumar et al.[16] compared three different techniques for MoS$_2$ synthesis in: a) sulphur vapour, b) H$_2$S/Ar gas and c) H$_2$S/Ar plasma. The best results were obtained by plasma treatment, because only in this case, was the surface completely sulfurized to form highly crystalline MoS$_2$ (with a thickness of 16 nm).

In the papers mentioned above, the authors first prepared Mo-containing thin films, which were further

used for sulfurization. Herein, we report on the synthesis of MoS_2 using as-received molybdenum in pure H_2S plasma. In contrast to P. Kumar et al.[15] we used rather short treatment times.

2 EXPERIMENTAL PART

2.1 Plasma treatment

Molybdenum foil with a thickness of 0.05 mm (from Goodfellow) was cut into small pieces with a size of 8×8 mm². The samples were treated by hydrogen sulphide (H_2S) plasma created in a plasma reactor that consisted of a Pyrex-glass tube with a length of 80 cm and a diameter of 4 cm. A coil of 6 turns was mounted in the centre of the tube. The samples were mounted in the middle of the coil. The plasma was created by a radio-frequency (RF) generator coupled to the coil via a matching network. The generator operated at the standard frequency of 13.56 MHz and at the nominal power of 800 W, which allowed ignition of plasma in so called H-mode (concentrated plasma inside the coil). The discharge tube was pumped with a rotary pump operating at the nominal pumping speed of 80 m³ h⁻¹. Pressure of H_2S gas was set to 20 Pa. The samples were treated for different periods from 2 s to 120 s. The samples quickly heated up and became red hot already after 2 s of treatment. Therefore, one sample was also treated by pulses to prevent overheating. Four pulses with a duration of 2 s were applied and the results were compared with a sample treated for 8 s. Additionally, one sample was also treated for 30 min at a low power of 150 W to avoid the sample heating by plasma. Instead, a heater was used to keep the sample temperature constant at 400 °C.

2.2 Surface characterisation

XPS characterization of the samples was performed to determine their surface chemical changes after plasma sulfurization. An XPS instrument model TFA XPS from Physical Electronics was used. The samples were excited with monochromatic Al-$K\alpha_{1,2}$ radiation at 1486.6 eV over an area with a diameter of 400 μm. Photoelectrons were detected with a hemispherical analyser positioned at an angle of 45° with respect to the normal of the sample surface. XPS survey spectra were measured at a pass-energy of 187 eV using an energy step of 0.4 eV, whereas high-resolution spectra were measured at a pass-energy of 23.5 eV using an energy step of 0.1 eV. The measured spectra were analysed using MultiPak v8.1c software from Physical Electronics, which was supplied with the spectrometer.

To estimate the sulphur film thickness, depth profiling of the selected sample with the maximum sulphur content was performed. A beam of Ar⁺ ions with an energy of 1 keV and at an incidence angle of 45° was used for sputtering over an area of 3 mm × 3 mm. This resulted in a sputtering rate of about 1 nm/min. XPS con-centration profiles were evaluated using the relative sensitivity factors from the manufacturer's handbook.

3 RESULTS AND DISCUSSION

Table 1 shows the XPS surface composition of the samples. For the untreated sample, carbon, oxygen and molybdenum were found. The concentration of carbon was rather high, which was a consequence of the surface contamination. The presence of oxygen with the O/Mo ratio ~ 3 indicates that the surface was oxidized and consisted of MoO_3 as it will be shown later. For the plasma-treated samples, concentrations of carbon and oxygen were significantly reduced, and additionally, sulphur appeared. In general, three different situations can be observed in **Table 1** regarding the treatment time. The samples treated up to 15 s had quite high sulphur and very low oxygen contents. The samples treated between 20 s and up to 60 s had low sulphur but high oxygen content. Whereas the samples treated for 90 s or more had only negligible amount of sulphur and very high content of oxygen.

The maximum sulphur concentration (almost 36 % of amount fractions) was found already at 2 s of treatment. As already mentioned, with the increasing treatment time the sulphur concentration decreased and became negligible at treatment times = 90 s. This variation of the sulphur content with treatment time is also shown in **Figure 1**, where the S/Mo ratio is displayed. The maximum ratio at 2 s of treatment was 0.96. By considering the theoretical S/Mo ratio in MoS_2 (S/Mo = 2), we could roughly estimate the relative content of MoS_2, which was 51 %.

For the oxygen, the opposite variation with treatment time was observed in comparison to the sulphur. At the beginning, the initial oxygen concentration at first significantly decreased and reached the lowest concentration of approximately 6 % of amount fractions. Then it started to increase with time and for the longest treat-

Table 1: XPS surface composition of the molybdenum samples treated in H_2S plasma

Time (s)	C (a/%)	O (a/%)	S (a/%)	Mo (a/%)	S/Mo	O/Mo
0	53.9	34.8	/	11.3	/	3.07
2	25.7	6.6	33.1	34.6	0.96	0.19
5	36.1	6.9	23.8	33.2	0.72	0.21
8	32.7	6.0	23.8	37.5	0.63	0.16
15	34.0	8.6	18.1	39.4	0.46	0.22
20	33.8	19.5	11.8	35.2	0.34	0.55
30	33.8	19.0	14.5	32.6	0.45	0.58
60	35.1	29.1	6.7	29.1	0.23	1.0
90	36.5	45.1	0.3	18.1	0.02	2.5
120	28.7	48.0	1.5	21.8	0.07	2.2
4 s × 2 s (pulsed)	31.0	8.2	26.1	34.8	0.75	0.23
30 min at 400 °C	44.3	33.1	8.8	13.8	0.64	2.4
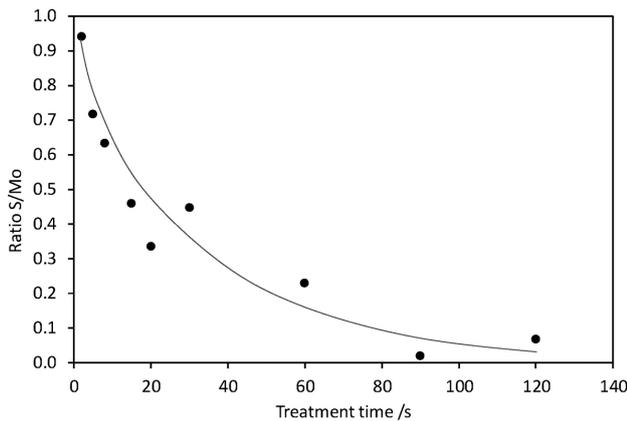
Figure 1: Variation of S/Mo ratio with treatment time

ment time, the concentration of oxygen exceeded the value for the untreated sample.

Figure 2 shows selected XPS spectra of Mo 3d and S 2s for the sulfurized molybdenum films. The molybdenum 3d spectrum appears as a doublet consisting of Mo 3d$_{5/2}$ and Mo 3d$_{3/2}$ peaks. For the untreated sample Mo 3d$_{5/2}$ and Mo 3d$_{3/2}$ were positioned at 232.6 eV and 235.8 eV, respectively, and corresponded to MoO$_3$ oxide, which is in agreement with the O/Mo ratio in **Table 1** and **Figure 3a**). After sulfurization for treatment times up to 15 s (samples with the highest sulphur concentrations), the main peak Mo 3d$_{5/2}$ was shifted to 229.3 eV, which was a consequence of the MoS$_2$ formation. This will be discussed later in more details. Mo 3d$_{3/2}$ at 235.8 eV almost disappeared, meaning that MoO$_3$ has vanished. Furthermore, the S 2s peak appeared as well. For treatment times between 20 s and 60 s, a small peak of Mo 3d$_{3/2}$ at 235.8 eV belonging to MoO$_3$ appeared again, because for these samples the concentration of oxygen prevailed over the sulphur concentration according to **Table 1**. At the longest treatment times (90–120 s), where the concentration of sulphur was negligible and the concentration of oxygen was again very high, the
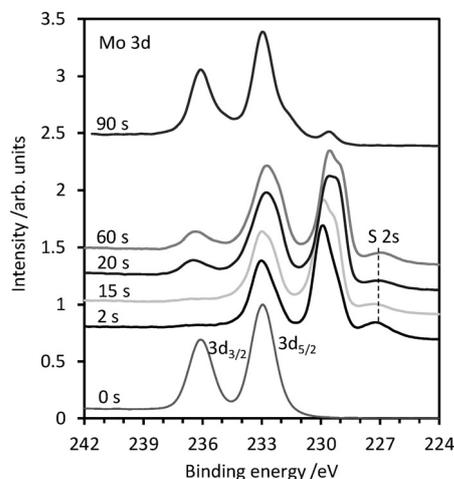
Mo 3d peak became similar to the one measured for the untreated sample.

A more detailed deconvolution of the Mo 3d peaks is shown in **Figure 3**. The spectra were fitted with the minimum number of peaks necessary to get the best matching. Here we should stress that during the reduction of MoO$_3$ (Mo^{6+}) oxide in plasma, oxides with the lower oxidation state (like MoO$_2$) can be formed as well. Unfortunately, the MoO$_2$ (Mo^{4+}) peak overlaps with the MoS$_2$ (Mo^{4+}). Furthermore, also 3d$_{5/2}$ of Mo^{6+} in MoO$_3$ overlaps with 3d$_{3/2}$ of Mo^{4+}, which makes the chemical quantification of the XPS spectra difficult. Because of a lack of oxygen on the sample treated for 2 s, the Mo^{4+} peak in **Figure 3b** was mostly attributed to the formation of MoS$_2$.[15] The corresponding sulphur S 2p peak for this sample is shown in **Figure 4**. The S 2p$_{3/2}$ peak at 162.2 eV corresponds to S^{2-}, thus confirming the formation of MoS$_2$. No elemental sulphur at 164 eV was found.

For the sample treated for 20 s which contained more oxygen, the Mo^{4+} peak can be attributed to both MoS$_2$ and MoO$_2$ (**Figure 3c**). Furthermore, an additional peak at 231.5 eV was necessary to include to obtain a good fit. This peak was assigned to the Mo^{5+} state, which was also reported by Spevack.[17] Moreover, also the Mo spectrum of the sample treated for 90 s, which was similar to the untreated one, contained some presence of Mo^{5+} and Mo^{4+} species (**Figure 3d**). A peak belonging to pure Mo^0 at 227.9 eV was not observed on any of the samples.

According to the literature, high temperatures and long treatment times are desirable for the formation of high-quality stoichiometric MoS$_2$ films. Therefore, it was surprising that the sulphur concentration was decreasing with treatment time (in our case, the longer treatment

Figure 2: High-resolution XPS spectra of molybdenum for different treatments
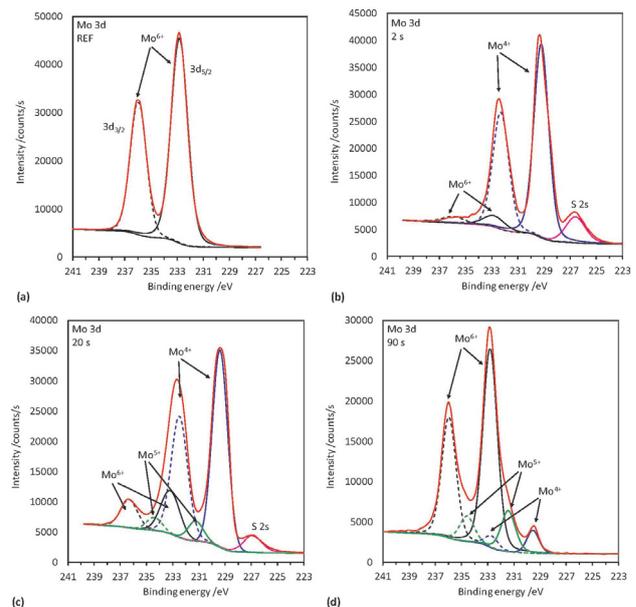
Figure 3: Detailed high-resolution XPS spectra of: a) the untreated sample and plasma-treated samples b) 2 s, c) 20 s and d) 90 s
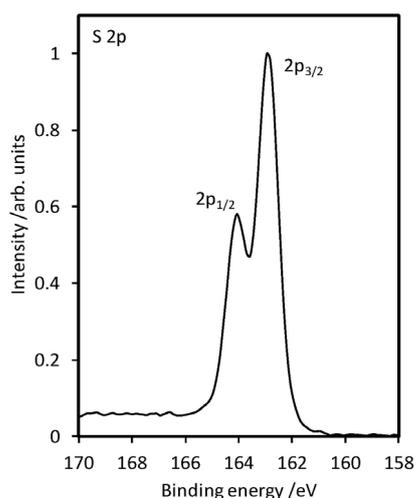
Figure 4: High-resolution XPS spectrum of sulphur for the sample treated for 2 s

times also caused the higher surface temperature). Therefore, one sample was treated in pulses to prevent overheating (shown in **Table 1**). It can be observed that the S/Mo ratio for this sample was higher than for the corresponding sample that was treated for the same time at once. It seems that at higher temperatures, MoS_2 became unstable. To further explore this observation, we treated one sample in mild plasma conditions to avoid heating by plasma. Instead, a heater was used to maintain the sample temperature constant at 400 °C (this was the maximum temperature obtained by the heater). The treatment time was set to 30 min to have more similar time conditions as in the published literature presented in the Introduction. Although the amount of sulphur (in *a/%*) appeared to be quite small, the ratio S/Mo was quite high. The apparently low sulphur concentration was a consequence of a relatively high carbon content (and also oxygen). As it will be shown later, the high carbon content was a consequence of the surface contamination. Nevertheless, we can conclude that a too high temperature might be detrimental and this explains a decrease in the sulphur with treatment time.

To estimate the sulphur film thickness, we performed XPS depth profiling of some selected samples, which are shown in **Figure 5**: a) for the as-received sample, b) for the sample with the maximum sulphur content (treated 2 s), and c) for the sample treated 30 min at 400 °C. For the untreated sample (**Figure 5a**), two oxidized layers can be observed. The upper one belonging to the MoO_3 oxide, with a thickness of about 5 nm (taking into account the etching rate of approximately 1 nm/min) and the lower one, where some oxygen still persisted and extended far into the depth. For the sample treated for 2 s (**Figure 5b**), a reduction of the oxygen concentration was observed. Furthermore, the sulphur appeared only in a very thin layer at the surface with a thickness of approximately 5 nm. The sulphur layer on the sample treated for 30 min was only slightly thicker. Furthermore, the high oxygen concentration found on the surface
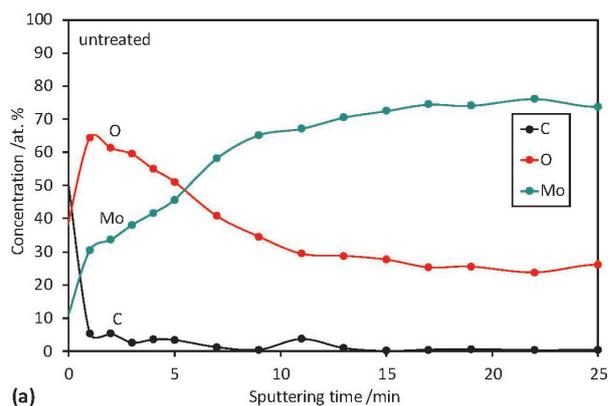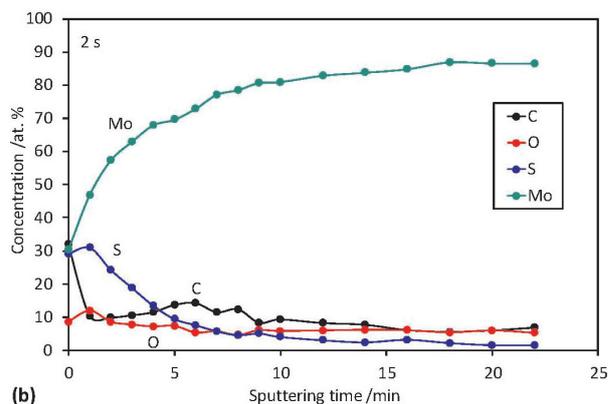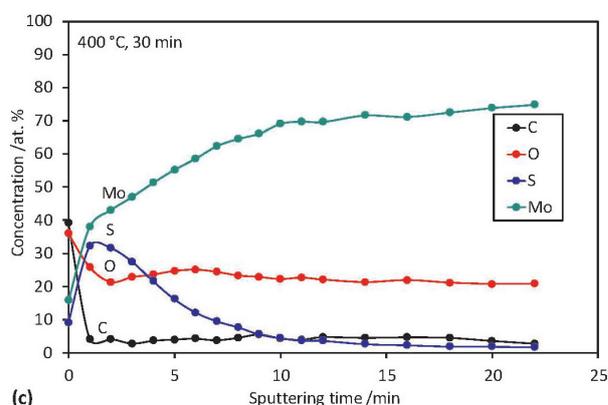
Figure 5: XPS depth profile of: a) the untreated molybdenum sample, b) the sample treated for 2 s and c) the sample treated for 30 min at 400 °C

(**Table 1**) extended well into the bulk, meaning that it was not just the surface oxidation. In contrast, the carbon was found only at the surface, which was explained as a surface contamination from the heating device.

4 CONCLUSIONS

As-received MoO_3 samples were treated for various periods in H₂S plasma created by a RF generator at 800 W. At 800 W the plasma was running in H-mode, which allowed for extensive sample heating. Already at the shortest treatment time (2 s) the sample was red hot. This sample had the maximum sulphur concentration (33 %

of amount fractions), whereas the oxygen content was very small only 6.6 % of amount fractions (initially ~ 35 % of amount fractions). This result showed that oxygen was replaced by sulphur, leading to the formation of MoS_2, as proved by the high-resolution XPS spectra as well. With the increasing treatment time, the sulphur concentration gradually decreased and became negligible at 90 s of treatment. Although high temperatures are desirable for a high-quality formation of MoS_2, it is possible that under our treatment conditions the MoS_2 was unstable and thus it decomposed.

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