

# MoS<sub>x</sub> Thin Films by Thermolysis of a Single-Source Precursor

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**Abstract.** Thin films of MoS<sub>x</sub> have been prepared on silicon substrates by spin coating and thermolysis of 0.5 M solutions of alkyldiammonium tetrathiomolybdates in 1,2-ethanediamine (EDA) and 1,2-propanediamine (12PDA). The films have been heat treated in air at temperatures between 80 and 250°C and under N<sub>2</sub> atmosphere at temperatures between 300 and 800°C. X-ray diffraction shows a restricted crystallisation and amorphous residues in both kinds of films. EDA-based films exhibit a high tendency to crystallise whereas 12PDA-based films form associated structures with the solvent preventing precursor crystallisation. An insight into the processes occurring in film formation is gained by infrared spectroscopy which indicates a beginning of the decomposition of the 12PDA-based film at temperatures as low as 80°C with incorporation of the diamine solvent. In contrast, the EDA-based films show first signs of a decomposition at 150°C. The decomposition of the intermediate MoS<sub>3</sub> in both cases starts between 250 and 300°C. By means of SNMS depth profiles carbon contents up to 21 and 32 atom-% were found in EDA- and 12PDA-based films, respectively. The films show a significant deficit of sulphur which is compensated by the carbon. Near the surface of the coatings a loss of carbon is observed.

**Keywords:** MoS<sub>x</sub>, thin film, liquid film coating, thermolysis, morphology

## 1. Introduction

Molybdenum disulphide (MoS<sub>2</sub>) plays an important role as a solid lubricant [1] and as a hydrodesulphurisation catalyst [2] and moreover its semiconducting properties make it a promising candidate for thin film solar cells [3]. MoS<sub>2</sub> thin films have been prepared by a variety of techniques including PVD [4] and CVD methods [5], deposition from chemical solution [6] and electrodeposition [7]. Nevertheless, it would be desirable to have liquid film techniques to deposit such films.

We have already reported on the deposition of MoS<sub>x</sub> thin films by thermolysis of single-source precursors deposited by liquid film coating [8]. The method, known as the metal-organic deposition (MOD) [9, 10], is widely used for the preparation of oxidic and metallic thin films and offers a wide range of deposition techniques like dip and spin coating, spray coating, and

screen printing. Though the MOD is increasingly used for the deposition of chalcogenide thin films [11], only little is known about the process of film formation.

In this contribution we elucidate the formation of MoS<sub>x</sub> thin films prepared by thermolysis of spin cast solutions of single-source precursors in organic diamines.

## 2. Experimental

Thin films of MoS<sub>x</sub> have been prepared on (100)-silicon substrates (35 × 35 mm<sup>2</sup>, 0.5 mm thick) from solutions of tetrathiomolybdates in organic diamines. Deposition solutions have been prepared by dissolution of (NH<sub>4</sub>)<sub>2</sub>MoS<sub>4</sub> (0.5 mol/l) in 1,2-ethanediamine (EDA) and 1,2-propanediamine (12PDA) and removal of the formed NH<sub>3</sub> under reduced pressure (100 mbar) [8].

The precursor films have been deposited by spin coating under ambient conditions at 2000 rev./min

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during 1 min. The highly viscous orange films were dried in air at temperatures from 80 to 250°C in a convection furnace. For a completion of the thermolysis, the samples were subsequently heat treated under inert N<sub>2</sub> atmosphere during 1 h at temperatures from 300 to 800°C.

The coatings were characterized by FTIR-transmission spectroscopy in the spectral range between 400 and 4000 cm<sup>-1</sup> under vacuum conditions (IFS 66v, Bruker) against a silicon reference. X-ray diffraction (XRD) has been performed under a grazing incidence of 2.0° in the 2 $\Theta$  range from 8 to 65° (Siemens D500). Depth profiles of the chemical composition were obtained by secondary neutral mass spectroscopy (SNMS).

### 3. Results and Discussion

#### 3.1. Structural Investigation

The structural evolution of film morphology with the temperature has been investigated by XRD (Fig. 1). After drying at 100°C, the EDA-based film shows the diffraction pattern of the pure crystalline ethylenedi-ammonium tetrathiomolybdate whereas the 12PDA-based film is amorphous with only a broad scattering at low 2 $\Theta$  values. At 300°C the EDA-based film becomes amorphous and at higher temperatures a broad peak arises at 13.3° corresponding to the (002) peak in the 2H-MoS<sub>2</sub> structure. The peak intensity further increases at 800°C and the peak becomes sharper with a maximum at 14.0° and a shoulder at lower 2 $\Theta$  values.

In contrast, the 12PDA-based films show a broad scattering background even up to temperatures of 800°C. At 600°C a weak diffraction is observed at approx 15°. On further heating the broad diffraction shifts and a second peak at 10.4° arises additionally to the weak (002) peak at 13.8°.

In both cases the low 2 $\Theta$  values for the (002) peak and the missing of (*hk*0) peaks indicate a restricted crystallisation in the 2H-MoS<sub>2</sub> structure with amorphous phases remaining especially in the case of the 12PDA-based films.

#### 3.2. SNMS Depth Profiles

The chemical composition of the films has been analysed for samples after heat treatment at 800°C by SNMS depth profiles (Fig. 2). The profiles show an

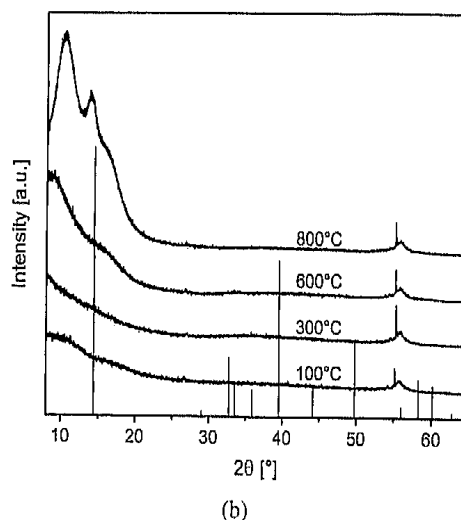
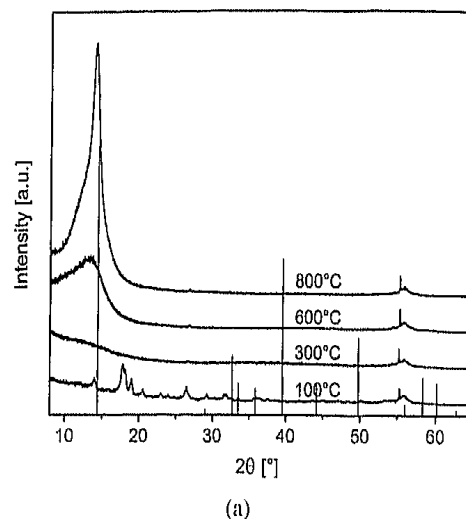
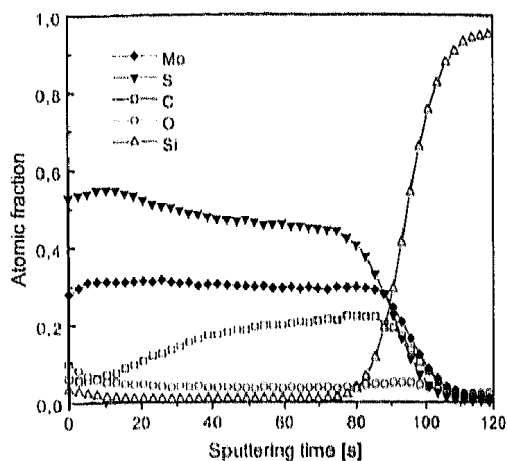


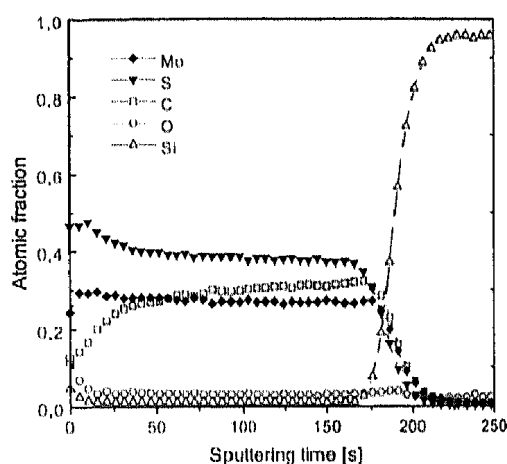
Figure 1. X-ray diffraction of (a) EDA- and (b) 12PDA-based thin films on silicon substrates after drying in air for 15 min (100°C) and after heat treatment under N<sub>2</sub> atmosphere for 1 h (300 to 800°C). The diffraction pattern of 2H-MoS<sub>2</sub> (JCPDS 37-1492) is given for comparison. The peaks at 55° stem from the silicon substrate.

8 to 10 nm thick surface layer with an increased oxygen content possibly due to adsorbed water or a partial oxidation. In the inner part of the coating the Mo and S contents are constant over a wide range with a S/Mo ratio of approx 1.5 in the EDA-based film and 1.4 in the 12PDA-based film. The carbon content increases slightly towards the substrate ending with values of 21 and 32 atom-%, respectively.

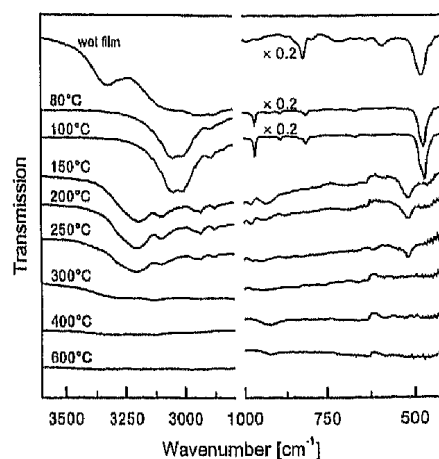
In between there is a region with a thickness of 30–40 nm which is characterised by a decreased carbon content accompanied by an increased sulphur content. In contrast, the atomic fraction of Mo appears to be constant over the whole film thickness. The molar ratio of S/Mo directly below the surface layer is 1.8 for the EDA-based film and 1.6 for the 12PDA-based film. The corresponding carbon contents are 6 and 2



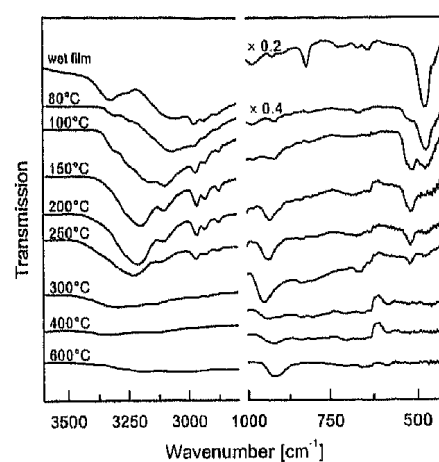
(a)



(b)



(a)



(b)

Figure 2. SNMS depth profiles for (a) EDA- and (b) 12PDA-based thin films on silicon substrates after heat treatment at 800°C under N<sub>2</sub> atmosphere for 1 h. The thickness of the films is 86 and 142 nm, respectively.

Figure 3. FTIR transmission spectra of (a) EDA- and (b) 12PDA-based thin films on silicon substrates after deposition (wet film), after drying in air (for 15 min (80 to 250°C) and after heat treatment under N<sub>2</sub> atmosphere for 1 h (300 to 600°C).

atom-%, respectively, suggesting a surface near diffusive evaporation of carbon during heat treatment. In both films the composition shows a significant sulphur deficit which is probably compensated by the excess carbon. The presence of a low but constant oxygen impurity probably can be explained by a water uptake and subsequent hydrolysis during deposition.

### 3.3. Investigation of the Thermolysis

An insight into the processes occurring during thermolysis of the spin-cast solutions can be gained from the FTIR transmission spectra given in Fig. 3. The cast liquid films show both characteristic bands of the liquid diamine ( $\nu(\text{NH}_2)$  at 3320 and 3250 cm<sup>-1</sup>) and of the broad bands of the diammonium salt in the region be-

tween 3200 and 2500 cm<sup>-1</sup> [12]. At 475 cm<sup>-1</sup> the strong  $\nu(\text{Mo-S})$  can be observed.

The EDA-based films (Fig. 3(a)) crystallise on drying at 80 and 100°C and show the spectrum of the pure diammonium salt with  $\nu(\text{NH}_3^+)$  at 3048 cm<sup>-1</sup> and typical overtones between 3000 and 2000 cm<sup>-1</sup>. The  $\nu(\text{Mo-S})$  band at 476 cm<sup>-1</sup> appears intense and with a narrow band width. Higher temperatures lead to a partial decomposition as seen by the decrease of the  $\nu(\text{Mo-S})$  vibration and the appearance of a new band at 515 cm<sup>-1</sup> which can be attributed to the  $\nu(\text{S-S})$  vibration of MoS<sub>3</sub> [13]. The decomposition of MoS<sub>3</sub> seems to be accomplished at 300°C as indicated by the missing  $\nu(\text{S-S})$  vibration. Another evidence for the decomposition of the diammonium salt comes from the vanishing of the  $\nu(\text{NH}_3^+)$  vibration and the appearance of vibrations at 3194 and 3099 cm<sup>-1</sup>. The  $\nu(\text{CH}_2)$

bands around  $2900\text{ cm}^{-1}$  show up to  $250^\circ\text{C}$  with nearly no shift suggesting a stability of the diamine in the film to at least  $250^\circ\text{C}$ . The formation of  $\text{MoS}_2$  could not be observed on the basis of the band at  $470\text{ cm}^{-1}$  that has been assigned to poorly crystalline  $\text{MoS}_2$  [13].

A different behaviour can be found in the decomposition of the 12PDA-based films (Fig. 3(b)). Here as well a diammonium salt is formed but the film still shows the  $\nu(\text{NH}_2)$  vibration of the diamine solvent at about  $3300\text{ cm}^{-1}$  up to  $100^\circ\text{C}$ . At  $80^\circ\text{C}$  the  $\nu(\text{Mo}-\text{S})$  starts to become weaker and a new vibration appears at  $520\text{ cm}^{-1}$  which accounts for an early decomposition of the 12PDA-compound and the formation of  $\text{MoS}_3$ . This decomposition seems to end at  $150^\circ\text{C}$  as indicated by the vanishing of the  $\nu(\text{Mo}-\text{S})$  and the appearance of a strong  $\nu(\text{S}-\text{S})$  vibration. As in the case of the EDA-based film, the  $\nu(\text{S}-\text{S})$  vibration disappears at temperatures higher than  $250^\circ\text{C}$  without appearance of the  $470\text{ cm}^{-1}$  band. The constant  $\nu(\text{CH}_2/\text{CH}_3)$  vibrations around  $2900\text{ cm}^{-1}$  indicate the presence of organic residues in the films at  $250^\circ\text{C}$ . Still uncertain is the origin of the broad peak in the region between  $900$  and  $1000\text{ cm}^{-1}$  but it could be due to  $\nu(\text{C}-\text{C})$  vibrations.

#### 4. Conclusions

Thin films of  $\text{MoS}_x$  have been prepared by liquid film coating from solutions of a single-source precursor. The films show different carbon contents and morphologies depending on the solvent and hence on the precursor used for its deposition. EDA-based precursor films show a distinct tendency to crystallise and are stable below  $150^\circ\text{C}$  whereas 12PDA-based precursor films can only be prepared in the amorphous state and start to decompose at a temperature of  $80^\circ\text{C}$ . In the latter case this leads to the incorporation of solvent molecules resulting in an increased carbon content compared to films prepared from EDA. In both types of

films the crystallisation of  $\text{MoS}_2$  is restricted due to the large carbon content of up to 30 atom-%. The film stoichiometry obtained from SNMS depth profiles shows a large sulphur deficit that is probably compensated by carbon. Though an evaporation of carbon is observed at the film surface the region of a decrease in carbon content seems to be limited to the first 30 to 40 nm of the film.

#### Acknowledgments

This work was financed by the BMBF (2A67/03 N 9040) and the State of Saarland (Germany). The authors wish to thank the IFOS, Kaiserslautern, for the preparation of the SNMS depth profiles.

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