Liquid Film Deposition of Chalcogenide Thin Films

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Abstract. Thin films of MoS_x were prepared by liquid film deposition of MoS_4^{2-} solutions in 1,2-diaminoethane (en) and 1,2-diaminopropane (pn) and subsequent thermolysis at temperatures up to 800°C under N_2. As the coatings show a high carbon content of up to 30 at.% that influences the morphology and the physical properties, the precursor thermolysis and the solution properties were analysed in detail and correlated to the coating properties. A reduction of the intermediately formed MoS_3 by organic residues at approx. 300°C was made out as the main cause of the carbon contamination during the thermolysis of the precursor salts $(enH_2)MoS_4$ and $(pnH_2)MoS_4$, leading to an immobilisation of the organic carbon. In the corresponding solutions cations of the form $[RNH_2 \cdots H \cdots NH_2R]^+$ could be detected, that result in an incorporation of additional diamine with 3–4 molecules per MoS_4^{2-} ion in the wet films. This cross-linked structure on the one hand reduces the tendency of the precursor salts to crystallise and thus makes it easier to obtain amorphous precursor films, but on the other hand increases the content of organic residues before thermolysis.

Keywords: chalcogenide, thin film, liquid film deposition, solution structure, thermolysis

1. Introduction

The liquid film deposition of thin films is a flexible and low-cost alternative to conventional gas phase deposition techniques like PVD and CVD. It is characterised by the deposition of a precursor solution by wet chemical methods like dip, spin and spray coating or printing techniques, and a subsequent thermal treatment to yield the desired thin film material [1]. The liquid film deposition is mostly used to apply lacquers, but also oxide and metal films are deposited, where it is known as the metal-organic deposition (MOD) [2]. Moreover, it also offers a promising approach for the preparation of chalcogenide thin films. This has been shown for As_2S_3 dissolved in 1,2-diaminoethane [3, 4] and a variety of other materials using highly polar solvents like N,N-dimethylformamide [5].

The corresponding precursors are usually only characterised with regards to their thermal decomposition, whereas less attention is given to the properties of the used solutions. But interactions between the precursor and the solvent can influence the deposition behaviour severely. Beside advantageous changes like a lowering of the crystallisation tendency or a lowering of the oxidation sensitivity, there are some drawbacks that can result from such interactions. Among these are apparent changes like a lower solubility of the formed compound or adduct, respectively, or a redox reaction, but also hidden changes like the increase of the organic content in the resulting coating. As the chemical composition of the precursor is often changed in solution, its decomposition behaviour might be affected as well.

We already reported earlier on the spin deposition of MoS_x thin films from a solution of MoS_4^{2-} in alkyldiamines [6–8]. The resulting coatings were homogeneous but showed a high carbon content of 20 to 30 at.%. A detailed characterisation of precursor and solution properties was therefore undergone especially with regards to interactions, in order to elucidate the causes for these carbon residues. The obtained results can be used to tailor the precursor properties and

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its interactions with the solvent and thus can help to improve the coating quality.

2. Experimental

The used alkyldiammonium-thiomolybdates were prepared via a sulphidation reaction of MoO_4^{2-} or an ion exchange based on $(NH_4)_2MoS_4$ [9]. The compounds were analysed by DTA/TG using an SSC 5200 (SEIKO Instruments) with Al_2O_3 crucibles and a heating rate of 5 K/min in air, under inert N_2 or reducing forming gas atmosphere.

The solutions were prepared in concentrations from 0.1 to 2.0 mol/l by dissolution of $(NH_4)_2MoS_4$ (99.99%, Aldrich) in 1,2-diaminoethane (ethylendiamine, en) and 1,2-diaminopropane (racemic, propylenediamine, pn) (both puriss., Fluka) and removal of the formed NH_3 in vacuo (100 mbar) at room temperature. The analysis of the solution structure was mainly based on Raman spectra, that were recorded on a Fourier Raman system (RFS 100, Bruker) at a wavelength of 1064 nm and a laser power of 300 mW by accumulation of 512 spectra with a resolution of 4 cm^{-1}. The solutions were kept in fused silica cells (5 mm) with a mirror at the back side (180°-geometry). For the thermal analysis 0.5 M solutions were reduced to low volume at 50°C and 20 mbar during 4 h. The obtained mushy residues were then immediately submitted to a combined DTA/TG under the same conditions as described above.

Liquid films of the precursor solutions were deposited from 0.5 molar solutions on various glass, ceramic and metal substrates with sizes up to 100×100 mm^2 by spin coating at 20°C and 40% RH with 2000 rev./min during 1 min. The viscous orange coloured films were dried in air at temperatures of up to 250°C in a convection furnace. Subsequently, the samples were heat treated under inert N_2 atmosphere during 1 h at temperatures up to 800°C to complete the thermolysis of the precursor.

3. Results and Discussion

3.1. *Precursor Thermolysis*

The precursor salts $(enH_2)MoS_4$ and $(pnH_2)MoS_4$ were analysed thermally under oxidative, inert and reducing atmosphere (Fig. 1). The onset temperature of decomposition in all atmospheres is approx. 170°C for the en-salt, whereas the pn-salt starts to decompose at

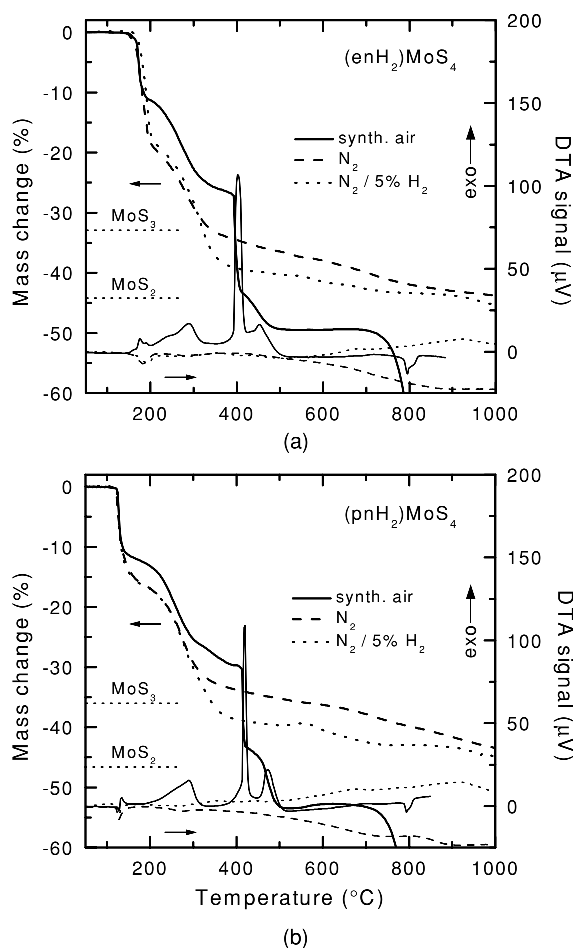

Figure 1. DTA/TG diagrams of (a) $(enH_2)MoS_4$ and (b) $(pnH_2)MoS_4$ in synthetic air, N_2 and forming gas (N_2/5 vol% H_2) with a heating rate of 5 K/min. The dotted lines at the left side mark the theoretical mass loss for MoS_3 and MoS_2, respectively.

120°C. The main reason for this difference is found in the racemic nature of the used pn that leads to a lower degree of order and hence to a lower thermal stability of the salt [9].

In air the shape of the decomposition curves is similar for both salts with a second decomposition step between 200 and 300°C. At approx. 390 and 410°C, respectively, the formed molybdenum sulphides start to be oxidised to MoO_3 which then sublimes at temperatures higher 700°C. The second exothermic peak between 400 and 500°C is most probably due to an oxidation of organic residues.

A comparison of the decomposition under inert and reducing atmosphere shows an identical shape up to temperatures of approx. 300°C for both salts. Such a

similarity is not found for the carbon-free $(NH_4)_2MoS_4$ [9, 10] where the decomposition under inert conditions starts at higher temperatures than under reducing conditions. It can therefore be assumed that in the case of the alkyldiammonium-salts, even under inert conditions, a reducing atmosphere is created by the organic residues comparable to that of the forming gas. This results in a reduction of MoS_3 to MoS_2 but also to an oxidation of the residues to carbon which then is immobilised. Between 300 and 400°C the mass loss is higher in forming gas which can be attributed to a volatilisation of carbon by reduction with H_2 again. Even at temperatures up to 1000°C the theoretical mass loss calculated for MoS_2 (see figures) is not reached due to carbon residues.

3.2. *Solution Structure*

In the liquid film deposition the described precursors are applied in form of their solutions in the corresponding diamine. The solutions were therefore analysed with regards to their internal structure, for which mainly Raman spectroscopy was used [9]. A shift of the $\nu(NH_2)$ band at $\approx$3300 cm^{-1} with the MoS_4^{2-} concentration can be observed, as shown in Fig. 2 for solutions in en and pn. In addition, a continuum below 3300 cm^{-1} with an increased intensity is found. The $\nu(MoS_4)$ bands at 480 to 450 cm^{-1} and $\delta(MoS_4)$ band at 180 to 190 cm^{-1} in contrast are almost unaffected by the concentration change.

A similar shift and continuum has been described by Dryjanski [11] for solutions of strong acids in 1,2-diaminoethane, which has been explained by the formation of easily polarisable cations of the form $[RNH_2 \cdots H \cdots NH_2R]^+$. Such cations are therefore postulated in the case of the MoS_4^{2-} solutions as well, with only little influence on the structure of the MoS_4^{2-} ions.

A similar behaviour of the solutions can be gathered from the DTA/TG diagrams of the solution residues in Fig. 3. In initial stages of the drying process, the surplus of diamine is evaporated until the mass loss curve follows that of the pure precursors. A striking feature is the lowering of the decomposition onset temperature for the en solution compared to that of the pure precursor, which is most probably caused by the amorphous structure of the intermediate diamine-rich compound.

Based on these results a structure of the MoS_4^{2-} solutions in alkyldiamines can be proposed, which is shown for en in Fig. 4. In addition to the intrinsic hydrogen bonds of the diamine (dotted lines) the network is linked via $[RNH_2 \cdots H \cdots NH_2R]^+$ cations (bold, dashed line), where the proton is stabilised via two diamine molecules. The MoS_4^{2-} units exist in an almost undistorted tetrahedral configuration with weak hydrogen bonds to diamine molecules (dashed lines) and a charge compensation by formation of contact ion pairs with the $[RNH_2 \cdots H \cdots NH_2R]^+$ cations. Due to the increasing cross-linking, the viscosity of the solutions increases strongly with the concentration of MoS_4^{2-} [9].

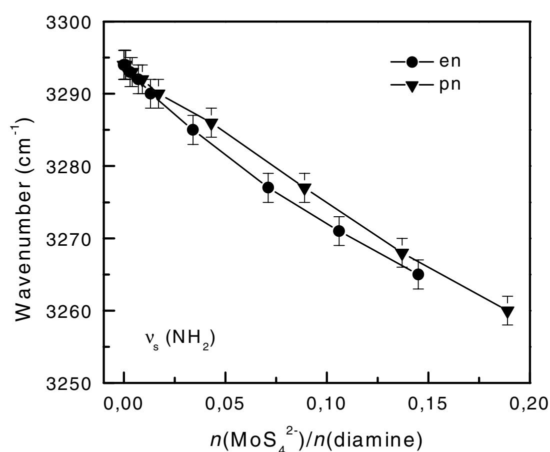

Figure 2. Position of the peak maximum of the $\nu(NH_2)$–Raman band in dependence of the molar ratio of MoS_4^{2-} to diamine for solutions in 1,2-diaminoethane (en) and 1,2-diaminopropane (pn).

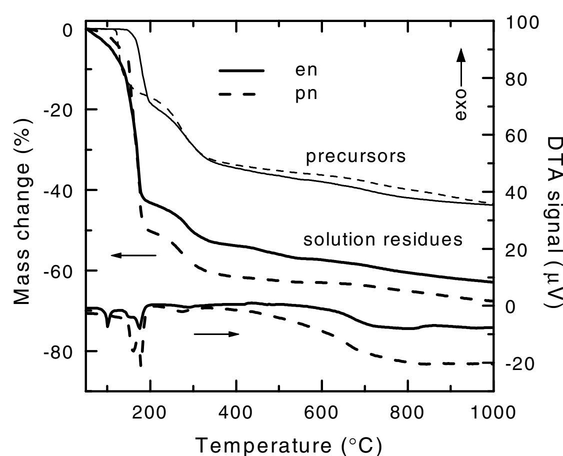

Figure 3. DTA/TG diagrams of the MoS_4^{2-} solution residues in 1,2-diaminoethane (en) and 1,2-diaminopropane (pn), together with the corresponding precursor salts under inert N_2 atmosphere with a heating rate of 5 K/min.

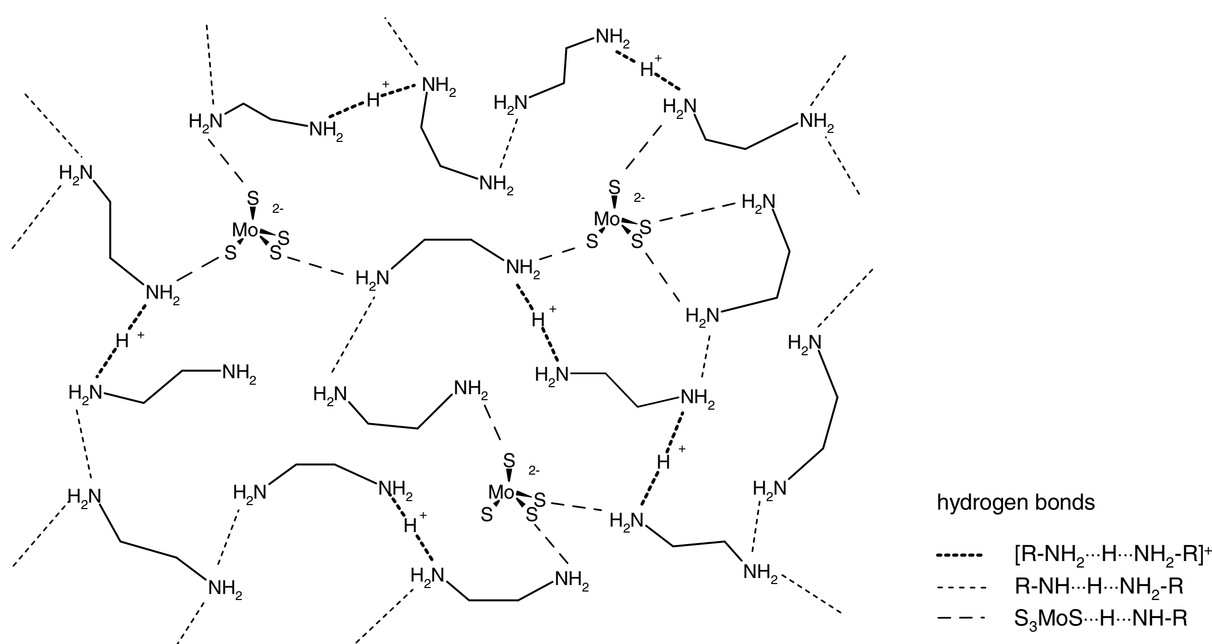

Figure 4. Schematic illustration of the solution structure of MoS_4^{2-} in 1,2-diaminoethane. The hydrogen atoms of the CH_2-groups are omitted.

3.3. Effects on Thin Film Properties

The applied liquid precursor films contain a large portion of surplus diamine compared to the pure precursor salts. Though this incorporation of diamine further increases the content of organics in the films, it seems to be an important pre-condition to obtain amorphous, homogeneous films without crystallisation of the precursor compound. Additionally, especially in the case of the en-salt a high heating rate during the initial drying is necessary to avoid a crystallisation [8], whereas the pn-salt always is obtained in the amorphous state from its solutions with surplus diamine incorporated due to its lower degree of order. As a consequence films prepared from solutions in pn always show a higher carbon content compared to en or 1,3-diaminopropane based coatings [9].

A fundamental drawback of the MoS_4^{2-}/diamine system, nevertheless, is the reduction of the MoS_3 by the organic residues, with the formed carbon being immobilised in the films. The resulting films hence contain up to 30 at.% of carbon as it could be shown by means of SNMS depth profiles [7]. As a consequence, the crystallisation of the MoS_2 is restricted to platelets with a length of approx. 4 nm even after heat treatment at 800°C. Despite these carbon impurities the frictional coefficient μ of such coatings deposited on stainless steel substrates is below 0.1 (measured against steel in air) [9].

4. Conclusions

The liquid film deposition of MoS_x thin films proved to be an interesting alternative to conventional vapour phase techniques. The used MoS_4^{2-}/diamine system forms stable solutions that can be applied easily to a variety of substrates, but it suffers from an increased carbon content in the films. This contamination is attributed to an immobilisation of carbon due to a redox reaction of the organic residues with MoS_x compounds. In the solutions, furthermore, a stabilisation of the proton via two diamine molecules was detected, resulting in an incorporation of surplus diamine in the dried viscous films. This reduces the crystallisation tendency of the precursor compounds but increases the content of organics and thus further increases the risk of carbon contamination.

For a cleaner decomposition it is necessary to find a precursor/solvent system that decomposes well below 300°C under formation of volatile fragments, in order to avoid a reduction of the MoS_x by the organics. Here the concepts of precursor design gathered in CVD can be helpful. A solvation of the precursor in its solutions

can be quite advantageous to obtain amorphous precursor films that can be then decomposed thermally.

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