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The effect of process parameters on the O/Mo ratio in laser deposition of molybdenum oxides from aqueous solutions

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Abstract

A study on precursor concentration (0.0075–0.050M), laser power (up to 210 mW) and scanning speed (from 0.15 to 1 mm/s) dependence of chemical composition of patterns deposited by pyrolytic laser decomposition of ammonium heptamolybdate is reported. Although the deposition parameters are varied over several orders of magnitude, the chemical composition of the deposits, as determined by energy and wavelength dispersive X-ray analyses, hardly varies. On setting low-temperature processing by applying either low power or high scanning speed, the oxidation state of molybdenum in the precursor is preserved, resulting in deposition of oxides of composition near to MoO₃. Using high power and low scanning speed, on the other hand, the attained higher temperatures initiate decomposition of ammonia, leading to partial reduction and yielding deposits of near-MoO₂ composition.

1. Introduction

As a result of recent studies on Ar⁺-laser-induced pyrolytic deposition from the liquid phase, using ammonium heptamolybdate as a model material, it has been found that a large variation in morphology and orders of magnitude differences in the amount of the deposited material can be obtained depending on deposition conditions [1,2].

The purpose of our current investigations is to obtain an insight into the processes governing pyrolytic liquid deposition. More specifically, the effect of deposition chemistry in determining the properties

of deposits is examined using complementary techniques, such as Scanning Electron Microscopy (SEM), Wavelength and Energy Dispersive X-ray Spectroscopy (WDS, EDS) and Selected Area X-ray Photoelectron Spectroscopy (SAXPS).

2. Experimental details

The substrates used are glass microscope slides covered with 130 nm vacuum-deposited tungsten. Lines are deposited by moving the Teflon sample holder perpendicularly to the vertically aligned Ar⁺ laser beam ($\lambda = 514.5$ nm) focused onto the substrate surface ($1/e^2$ diameter: $2w_0 = 4.4$ mm) through an approximately 1 mm thick solution layer of 0.0075–0.050M (NH₄)₆Mo₇O₂₄ · 4H₂O. The

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morphology of the deposited lines was examined by optical and electron microscopy (SEM).

Changes in the chemical composition of the deposits are followed by determining the O/Mo relative intensity ratio by combined SEM/EDS/WDS measurements using a JEOL JSM35 type microscope equipped with JEOL type wavelength dispersive and Kevex type energy dispersive X-ray spectrometers. A special aperture in front of the EDS detector allows simultaneous measurement of the MoL α and OK α lines. The relative intensity is calculated as $(O_{\ell} - O_b)/(Mo_{\ell} - Mo_b)$, from the oxygen and molybdenum intensities measured on the line (O_{ℓ} , Mo_{ℓ}) and on the tungsten substrate along the line as background (O_b , Mo_b). Comparison between different sets of measurements is ensured by calibration with pure sapphire and Mo standards:

$$O/Mo = [(O_{\ell} - O_b)/(Mo_{\ell} - Mo_b)] / [(O_{Al_2O_3} - O_{bg})/(Mo_{Mo} - Mo_{bg})],$$

where O_{bg} and Mo_{bg} denote the respective background intensities. The uncertainty in quoted O/Mo values is estimated to be 20%.

A CRATOS XSAM 800 photoelectron spectrometer, equipped with a 1 mm cone, was used for the SAXPS measurements. The sample was cooled by liquid nitrogen and kept in the chamber at a base pressure of $< 2.5 \times 10^{-9}$ Torr. Ten consecutive spectra were acquired (in 0.05 eV steps), using the MgK α (1253.6 eV) X-ray line as an exciting source, and averaged to follow the changes in the binding energy of molybdenum.

3. Results and discussion

As expected, the variation of precursor concentration, laser power and scanning speed changes the chemical composition of the deposited patterns. The dependence on laser power exhibits a biphasic character. As shown in Fig. 1 in the middle of the laser power range over which deposition is achieved (90–160 mW), the O/Mo ratios scatter between 0.5 and 1.0 which means that the O/Mo ratio is independent of both the precursor concentration and scanning speed within experimental error. Approaching both the lower and upper boundaries of the laser power

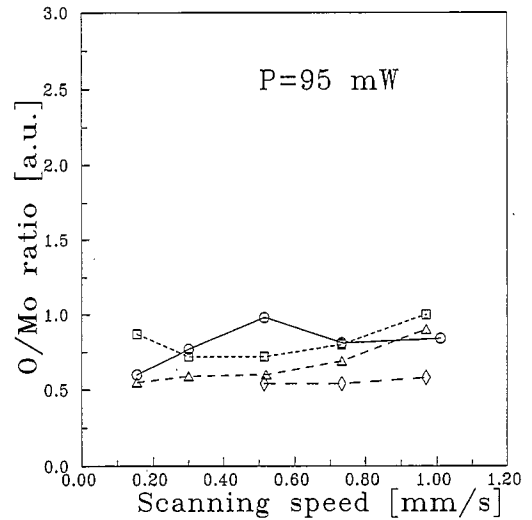


Fig. 1. O/Mo ratio as a function of the scanning speed at constant laser power (95 mW) and different precursor concentrations: (O) 7.5×10^{-3} M; (□) 10^{-2} M; (Δ) 2.5×10^{-2} M; (◇) 5×10^{-2} M.

range a dependence on scanning speed is obtained. As seen in Fig. 2 the O/Mo ratio increases with increasing scanning speed. The effect of the changes in the precursor concentration becomes apparent in these low and high power domains, as well (Fig. 3).

For low scanning speeds O/Mo values between 1/2 and 1 are obtained at any laser power and

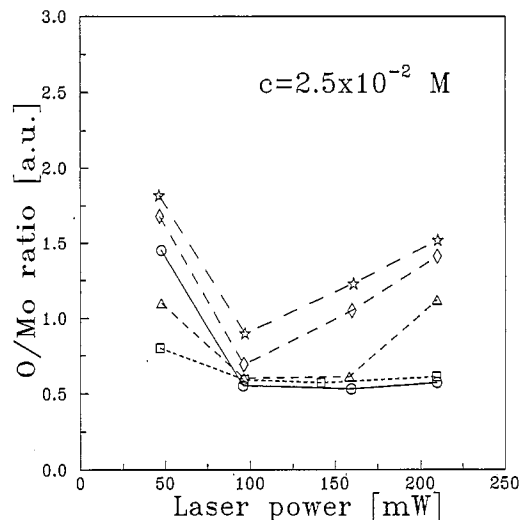


Fig. 2. O/Mo ratio as a function of the laser power at constant precursor concentration (2.5×10^{-2} M) and different scanning speeds: (O) 0.150 mm/s; (□) 0.290 mm/s; (Δ) 0.510 mm/s; (◇) 0.735 mm/s; (☆) 0.960 mm/s.

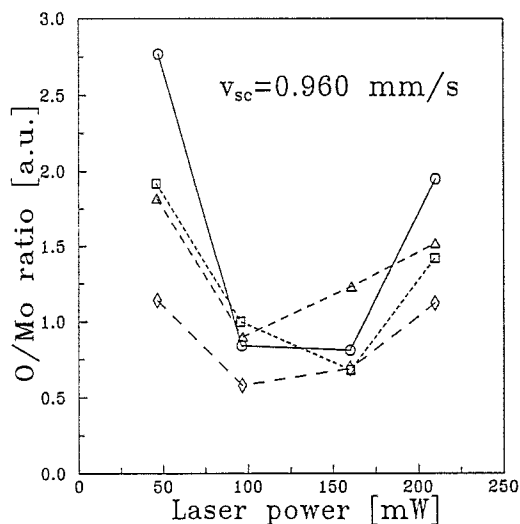


Fig. 3. O/Mo ratio as a function of the laser power at constant scanning speed (0.960 mm/s) and different precursor concentrations: (○) 7.5×10^{-3} M; (□) 10^{-2} M; (△) 2.5×10^{-2} M; (◇) 5×10^{-2} M.

concentration values. Fig. 3 shows how the variation of concentration influences the scale of changes in O/Mo ratio at high scanning speeds (0.96 mm/s). With increasing concentration the changes in O/Mo ratio caused by variations in processing power or writing speed are less.

As a result of SEM/EDS/WDS mapping of changes in chemical composition of the deposits as a function of laser power, scanning speed and precursor concentration two domains can be identified. At low powers (90–160 mW) the O/Mo ratio has a

minimum and is constant within experimental error over the whole concentration and scanning speed range investigated. In this range continuous, bulky stripes typically several μm in height are deposited [1–3]. Approaching the limiting values of the process parameter range, for $v_{sc} \geq 0.5$ mm/s, P at about 50 mW and $c > 10^{-2}$ M, gradually increasing O/Mo values characterize the continuous or dot-like [1], but always extremely thin (≤ 0.1 μm) lines [2,3]. Note that the lowest O/Mo ratios ($\sim 1/2$) have been measured on stripes possessing the characteristic volcano-like cross-section due to material depletion in the line centre.

The realization of the direct correlation between the O/Mo values and the thickness of the deposited patterns has prompted a re-examination of the EDS/WDS measurements and the evaluation process. Using the on-board simulation procedure the depth-dose functions of the $\text{OK}\alpha$ and $\text{MoL}\alpha$ radiations (Fig. 4) give a weighted penetration depth of approximately 0.6 μm for both radiations in bulk MoO_3 . The similarity of the two curves (Figs. 4b and 4c) guarantees that the measured O_i/Mo_i ratios are insensitive to changes in layer thickness. Although the 130 nm tungsten film provides effective shielding, when analysing oxide layers of thicknesses below ~ 0.1 μm , the majority of the $\text{OK}\alpha$ signal may arise from the glass support. This contribution is corrected by subtracting the substrate background signal, O_b . Consequently the evaluation procedure provides exact relative intensity values for line thicknesses below 0.6 μm . Since for thicknesses ≥ 0.6

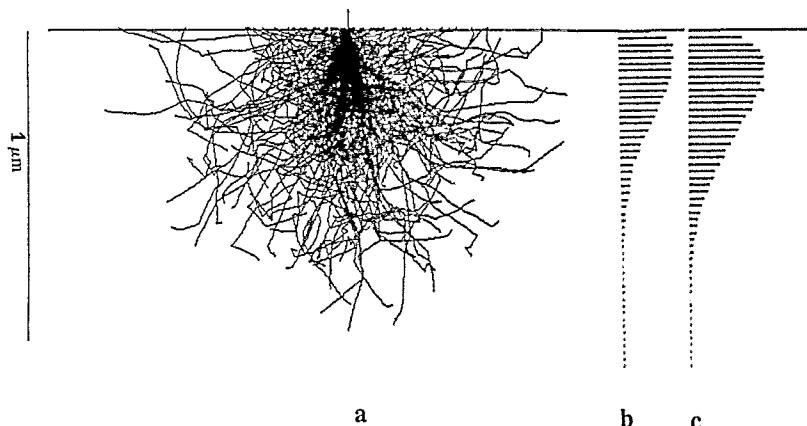


Fig. 4. Trajectory simulation in bulk MoO_3 (a) with $\text{MoL}\alpha$ (b) and $\text{OK}\alpha$ (c) X-ray depth-dose functions.

μm the measured O_{1s} signal does not contain any contribution from the glass support, the background correction applied results in slightly underestimated O/Mo values. This means that the results of the EDS/WDS analysis are correct, with slightly up-scaled absolute values.

Binding energies of 231.55 ± 0.05 eV have been measured by SAXPS for $\text{Mo}(3d_{5/2})$ in the deposits of minimum O/Mo ratio, which corresponds to an oxidation state of 4.66 ± 0.05 [4,5], the maximum being 232.65 eV (MoO_3). It is worth noting that the evaluation of the XPS data based on comparison of the normalized peak areas, which are proportional to the amount of the elements, indicates greater differences in the oxygen content of the deposits than those calculated from the oxidation states given by the peak positions.

The above results strongly suggest the definitive role of the temperature in controlling and allowing slightly different chemical pathways in pyrolytic laser decomposition of ammonium heptamolybdate. For low temperatures, attained with low power or high speed, the deposition is the result of thermal decomposition of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ preserving the oxidation state of Mo in the precursor, while at higher temperatures an additional reduction effect arising from the decomposition of ammonia shifts the stoichiometry of the deposited material nearer to MoO_2 .

4. Conclusions

Ar^+ -laser-induced pyrolytic decomposition of aqueous solutions of ammonium heptamolybdate brings about deposition of molybdenum oxides of composition between MoO_2 and MoO_3 . In spite of

the extensive variation of deposition parameters over several orders of magnitude, the chemical composition of the deposits hardly varies. Low power or high speed, i.e. low-temperature processing preserves the oxidation state of molybdenum in the precursor, resulting in deposition of oxides of composition near to MoO_3 . Applying high power or low scanning speed, the attained higher temperatures initiate decomposition of ammonia leading to partial reduction and yielding deposits of near- MoO_2 composition. The marginal effect of deposition parameters on the chemical composition of the deposits reveals that the deposition kinetics is controlled by the material transport [3] and not by the minor differences in deposition chemistry.

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References

- [1] K. Bali, Zs. Geretovszky, A.L. Tóth and T. Szörényi, *Appl. Surf. Sci.* 69 (1993) 326.
- [2] Zs. Geretovszky, L. Kelemen, K. Bali and T. Szörényi, *Appl. Surf. Sci.* 86 (1995) 494.
- [3] Zs. Geretovszky, T. Szörényi, K. Bali and A.L. Tóth, *Thin Solid Films* 241 (1994) 67.
- [4] W.E. Swartz, Jr. and D.M. Hercules, *Anal. Chem.* 43 (1971) 1774.
- [5] S.O. Grim and L.J. Matienzo, *Inorg. Chem.* 14 (1975) 1014.