Mixed-metal oxide films *via* a heterobimetallic complex as an MOCVD single-source precursor

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A single-phase polycrystalline mixed-metal oxide $WCoO_4$ film on Si(100) can be prepared by MOCVD with the use of $[(\eta\text{-}C_5H_5)(CO)_3WCo(CO)_4]$ as a single-source precursor.

Use of single-source precursors in the preparation of binary metal alloys or ceramic films has drawn much attention in recent years due to their potential to simplify engineering procedures.[1–8] Theoretically, a single-source precursor should contain the same stoichiometric metal content as in the final binary metal film. However, in most cases, films have metal ratios different from the precursor. This may be due to the decomposition of the precursor into individual metal fragments during the deposition process.[2,3,7]

A series of III–V single-source precursors with strong two-centre, two-electron bonds rather than donor–acceptor linkages were used to prepare III–V films.[6,9] In addition, complexes of the type $[L(CO)_nM\text{–}ER_2L']$ (M = d-block metal; E = Al, Ga, In; R = alkyl; L = CO, PR_3, $\eta\text{-}C_5H_5$; L′ = O, N Lewis-base donor) have been successfully employed as single-source precursors to prepare ME binary alloy films.[2,10,11] Most of them have the same metal ratio as in the precursors. However, attempts to prepare mixed transition-metal films with single-source precursors have always resulted in fragmentation of the complexes so that the films contain metal ratios different from the precursors.[2,3,7] The presence of an M–M′ bond in heterobimetallic complexes may avoid fragmentation during the deposition process. Herein, we report the use of $[(\eta\text{-}C_5H_5)(CO)_3WCo(CO)_4]$ **1**[12] as a single-source precursor for the preparation of $WCoO_4$ films.

Selection of **1** as a single-source precursor for the preparation of W–Co ceramic films is based on the following criteria: (*a*) $[W(\eta\text{-}C_5H_5)(CO)_3H]$ and cobalt carbonyl have been used as precursors for organometallic chemical deposition of W[13] and Co;[14,15] (*b*) these heterobimetallic complexes have the desired stoichiometry in terms of metal content and (*c*) the presence of a W–Co bond may impart stability to the complex so avoiding fragmentation during deposition.

The deposition was carried out in a horizontal hot-wall reactor. The deposition zone (a quartz tube) and substrate [Si(100)] were preheated under vacuum to the deposition temperature. The precursor reservoir was then heated to 60 °C in order to sublime the complex into the deposition zone. The deposition rate is *ca.* 80 Å min^{-1} at 300 °C. During deposition, the pressure of the system was in the range 250–500 Torr.

The film so obtained was amorphous as indicated by its powder X-ray spectrum. The morphology of the film was studied by AFM which indicated a relatively smooth surface with an average roughness of 5.0 Å. Both W and Co are evenly distributed in the film as shown by EDS mapping of the film. However, the Co/W ratio depends on the deposition temperature and is not necessarily unity as indicated by EDS analysis,† but ranges from *ca.* 1 (250–300 °C)‡ to 2 at 500 °C with higher deposition temperatures leading to higher Co content. This is understandable since vacuum degradation of single-source precursors in thin film deposition is kinetically controlled and depends on the deposition temperature.[1–3]

Pyrolysis of organometallic complexes containing cyclopentadienyl and CO ligands may result in the formation of metal carbide, metal oxide or amorphous carbon in the pyrolysis product.[16] In order to evaluate these possibilities, Auger spectra of the films were measured. Auger depth profile measurements (Fig. 1) indicate that the films contain carbon from the surface to the interface. However, only a small amount of oxygen, probably due to contamination, was present on the surface of the film.

In situ heating of the amorphous film with a Co/W ratio of 1 under oxygen at 900 °C produced a $WCoO_4$ film. The X-ray spectrum of the film showed that the film was polycrystalline (Fig. 2)§ and an AFM micrograph showed the grain size to be *ca.* 0.5 μm and the average roughness to be 380 Å (Fig. 3). Co and W were reasonably evenly distributed in the film as indicated by both EDS mapping and Auger depth profile. Only a small amount of carbon was detected on the surface of the film which may be due to contamination of the surface as supported by the Auger spectrum which indicates the absence of carbon after removing the contaminated surface upon sputtering (Fig. 4). This indicates that the amorphous carbon in the film was almost completely removed from the film upon oxidation.

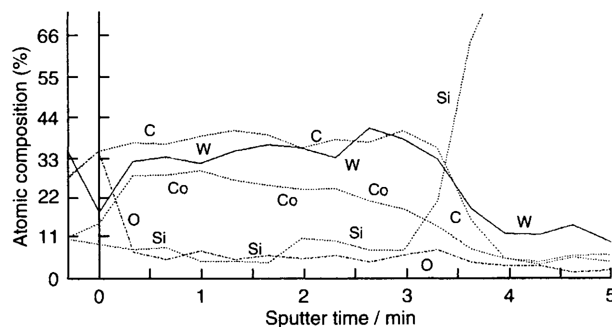

Fig. 1 Auger depth profile of CoWC amorphous film on Si(100)

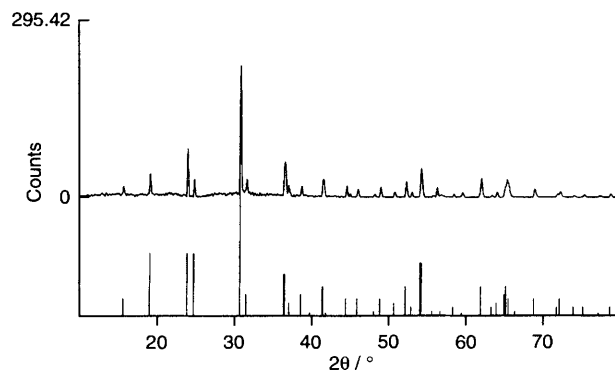

Fig. 2 Power X-ray diffraction spectrum of $CoWO_4$ polycrystalline film on Si(100). Diffraction pattern from the Powder Diffraction File, International Centre for Diffraction Data are also shown for comparison.

These results are encouraging for further development of heterobimetallic single-source precursors containing metal–metal bonds for binary alloys and ceramic films.

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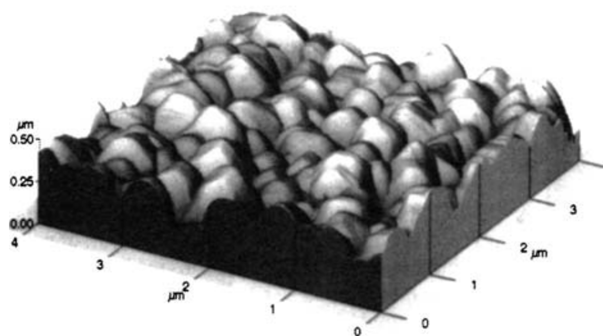

Fig. 3 Atomic force micrograph of the $CoWO_4$ film on Si(100)

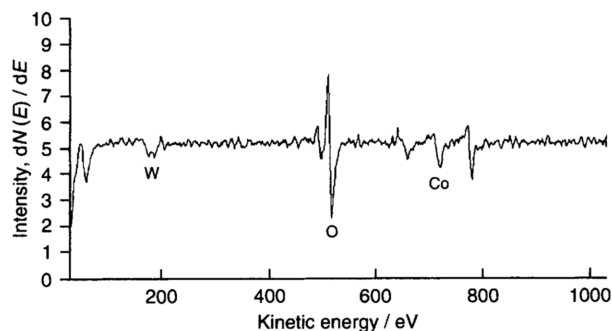

Fig. 4 Auger survey spectrum of $CoWO_4$ film on Si(100) after 20 min of Ar-ion sputtering

Footnotes

† Co/W ratio analysis by EDS: 1.16(5) at 250 °C, 1.15(5) at 300 °C, 1.60(9) at 400 °C, 1.92(10) at 500 °C; the ZAF method was used in the analysis, 10 data points were randomly obtained from each sample.

‡ For film deposited at 300 °C the Co/W ratio was 1.04 according to AAS and 1.07 by ICP–AES.

§ $WCoO_4$. Powder Diffraction File, International Centre for Diffraction Data, 1990; JCPDS No. 15-867. Strong lines. Calc. 2.92/*x*, 4.67/3, 3.73/3, 1.70/3, 2.47/2, 2.46/2, 2.19/1. Found: 2.91/*x*, 4.66/2, 3.72/4, 1.70/2, 2.46/3, 2.18/2.

References

1 T. Kodas and M. Hampden-Smith, *The Chemistry of Metal CVD*, VCH, New York, 1994, pp. 439–440.
2 R. A. Fisher, M. Kleine, O. Lehmann and M. Stuke, *Chem. Mater.*, 1995, **7**, 1863.
3 P. Doppelt and T. H. Baum, *Chem. Mater.*, 1995, **7**, 2217.
4 J. Cheon, J. Arnold, K. M. Yu and E. D. Bourret, *Chem. Mater.*, 1995, **7**, 2273.
5 F. Maury, L. Brandt and H. D. Kaesz, *J. Organomet. Chem.*, 1993, **449**, 159.
6 A.H. Cowley and R. A. Jones, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1208.
7 C. L. Czekaj and G. L. Geoffroy, *Inorg. Chem.*, 1988, **27**, 8.
8 C. Y. Narula, A. Varshney and U. Riza, *Chem. Vap. Deposition*, 1996, **2**, 13.
9 F. Maury, *Adv. Mater.*, 1991, **3**, 542.
10 R. A. Fisher, J. Behm, T. Priermeier and W. Scherer, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 746.
11 R. A. Fisher, J. Behm, T. Priermeier and W. Scherer, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 748.
12 H. B. Abrahamson and M. S. Wrighton, *Inorg. Chem.*, 1978, **17**, 1003.
13 K. K. Lai and H. H. Lamb, *Chem. Mater.*, 1995, **7**, 2284.
14 G. A. West and K. W. Beeson, *Appl. Phys. Lett.*, 1988, **53**, 740.
15 M. E. Gross, D. Schnoes-Krauz, D. Brasen and M. Luftman, *J. Vac. Sci. Technol. B.*, 1988, **6**, 1548.
16 T. Kodas and M. Hampden-Smith, *The Chemistry of Metal CVD*, VCH, New York, 1994, pp. 411–413 and references therein.

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