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Deposition of osmium and ruthenium thin films from organometallic cluster precursors

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Single-source organometallic precursors based on a number of homometallic clusters as well as heterometallic cluster $RuOs_3(CO)_{13}(\mu\text{-}H)_2$ have been used for the chemical vapor deposition of osmium films and osmium–ruthenium alloy films, respectively. Copyright © 2009 John Wiley & Sons, Ltd.

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Keywords: osmium; ruthenium; alloy; cluster; CVD

Introduction

Since Mond first reported the preparation of Ni films from $Ni(CO)_4$, the preparation of metallic thin films from organometallic compounds by chemical vapor deposition (CVD) has attracted considerable interest.[1] Osmium has a number of applications, for example, in the fabrication of gate material for high-*k* dielectrics, methane-detection chemical sensors, X-ray mask materials, thermionic cathodes and in the making of conductive coatings with good secondary electron emission efficiency.[2] In recent years, osmium or osmium oxide thin films with reasonable purity have been obtained from $Os(C_5H_5)_2$,[3] OsO_4,[4] $Os(CO)_5$,[5] $Os_3(CO)_{12}$,[6] $Os(CO)_4(CF_3C{\equiv}CCF_3)$,[7] *cis*-$Os(CO)_4I_2$, *fac*-$Os(CO)_3[OC(COCF_3)_2](O_2CCF_3)$,[8] $[Os(CO)_3\{3,5\text{-}(CF_3)_2\text{-}pz\}]_2$ and $Os_3(CO)_{10}(\mu\text{-}H)[3,5\text{-}(CF_3)_2\text{-}pz]$ (pz = pyrazole).[9] Since osmium clusters are air-stable at room temperature and have sufficient volatility to be transported in the vapor phase, they make possible precursors for the deposition of osmium thin films.

Herein, we describe the use of the osmium carbonyl complexes $[Os_3(CO)_{10}(\mu\text{-}H)][\mu\text{-}S(CH_2)_3Si_8O_{12}(i\text{-}butyl)_7]$ (**1**), $Os_2(CO)_6(\mu\text{-}I)_2$ (**2**) and $Os_3(CO)_{12}Br_2$ (**3**) as precursors for the deposition of osmium thin films, as well as the heteronuclear carbonyl cluster $RuOs_3(CO)_{13}(\mu\text{-}H)_2$ (**4**) to form an Os–Ru alloy thin film (Fig. 1). We originally prepared **1** as a possible molecular model to study the process of cluster decomposition on a silica surface. Clusters **2** and **3** were chosen as, together with the previous report on *cis*-$Os(CO)_4I_2$,[8] they would allow an examination into whether the cluster nuclearity has any effect on the metallic thin film morphology. Cluster **4** represented an opportunity to examine the use of heteronuclear clusters as a single source precursor for metallic alloy thin films.

Results and Discussions

To distinguish the samples obtained, samples obtained at a deposition temperature of 400 and 500 °C are denoted as **n**-400 and **n**-500, respectively, where **n** refers to the compound number of the precursor (**1** – **6**).

Deposition of Osmium Thin Films using 1, 2 or 3 as CVD Source

The TGA profiles for **1, 2** and **3** are shown in Fig. 2. Complex **1** showed a two-stage weight loss, the first between 90 and 300 °C, and the second starting from 300 °C, with a residual weight of 0.7% at 500 °C (calculated residual weight: 67%). The TGA profile for **2** showed weight loss taking place over a similar temperature range, with a final residual weight at 500 °C of ∼10% (calculated residual weight: 48%), while **3** exhibited decomposition over a much narrower range, decomposition being almost complete at ∼230 °C, to give a residual weight of ∼10% at 500 °C (calculated residual weight: 54%). The high molecular weights, especially of **1**, suggest that the low residual weights observed are unlikely to be due to volatility of the cluster precursors themselves but may be attributed to formation of more volatile species via partial ligand loss.

All the as-deposited osmium thin films were dark gray, lustrous and adhered well to the silicon surfaces. They were similar to those reported earlier.[3–9] The SEM images of the thin films are shown in Fig. 3; the EDX spectra show the presence of elemental osmium only. As is apparent from the SEM images, the morphology of the thin films varies with the precursor and temperature. However, in all cases, XRD analysis indicates a preferred orientation along the (002) direction (Fig. 4). This is interestingly different from that for *cis*-$Os(CO)_4I_2$, which was reported to show a preference for the (100) direction.[8] The reason for the difference is not clear, although it may have to do with the deposition method; with H_2 as carrier gas as opposed to vacuum deposition in our case. Aggregation into

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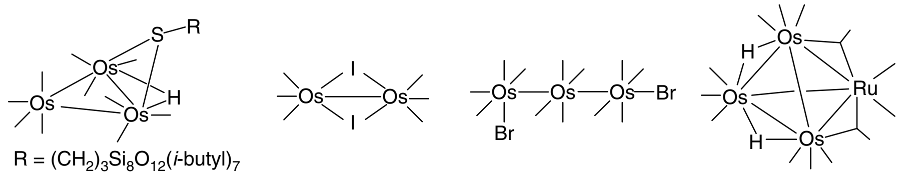

1 2 3 4

Figure 1. Molecular structures of carbonyl clusters **1–4**.

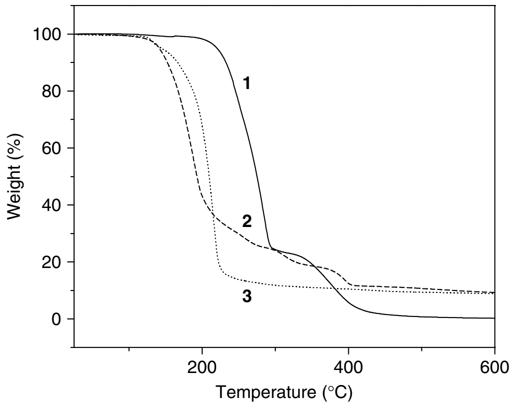

Figure 2. TGA profiles of complexes **1, 2** and **3**.

bigger spherical particles is observed at the higher deposition temperature, and is corroborated by the XRD results. For example, the XRD signals for **1**-500 are clearly broadened with respect to those for **1**-400, indicating a more amorphous structure comprising a randomly distributed, hexagonal close-packed osmium.

Deposition of an Os–Ru Alloy Thin Film using a Single-source CVD Precursor

The thin films deposited from **4** onto silicon wafers at 400 and 500 °C were well-adherent (they did not peel off upon ultrasonic cleaning, unlike gold films), and exhibited a dark gray metallic cast; the SEM images are depicted in Fig. 5. The thin film obtained at 400 °C was dominated by microcrystalline grains; a higher substrate temperature produced a relatively smoother morphology. The Os : Ru ratios for these films estimated from the EDX analyses were ∼1 : 1 and 6 : 1 for **4**-400 and **4**-500, respectively (Fig. S1).

That the films comprise alloys rather than physical mixtures of two discrete metals is corroborated by the XRD spectra. The (002) lines for **4**-400 and **4**-500 are observed as intense lines at 41.95° and 41.82°, which correspond to lattice constants of 2.152 and 2.158 Å, respectively. These lines lie in 2θ values

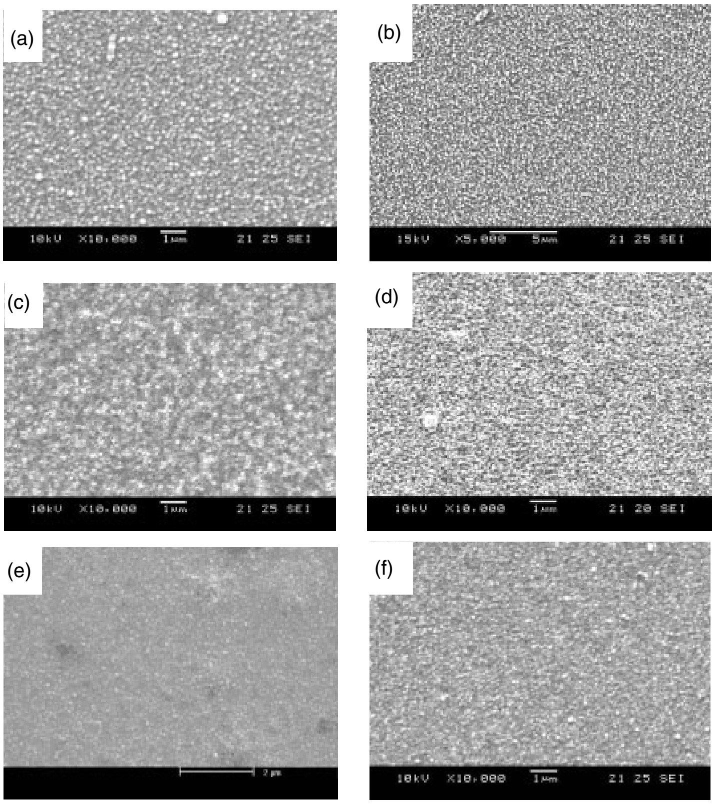

Figure 3. SEM images of the osmium thin films deposited on silicon wafer. (a) **1**-400, (b) **1**-500, (c) **2**-400, (d) **2**-500, (e) **3**-400 and (f) **3**-500.

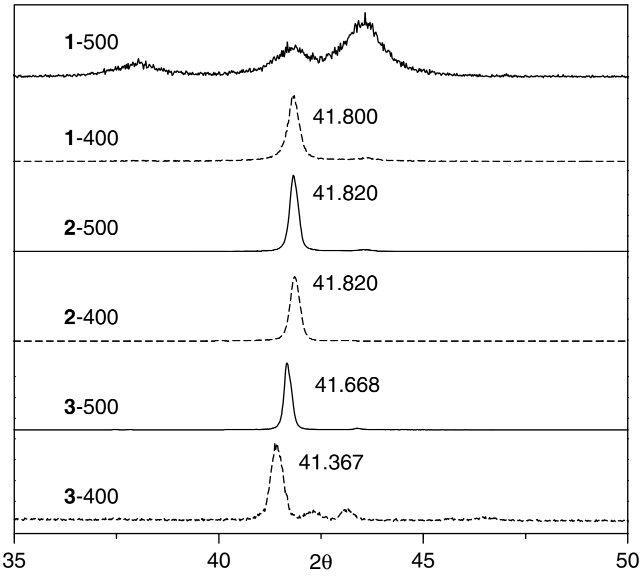

Figure 4. XRD patterns of the osmium thin films deposited on silicon wafer.

between those observed for the thin films obtained from the homometallic clusters $Os_3(CO)_{12}$ (**5**) and $Ru_3(CO)_{12}$ (**6**), which were also polycrystalline with a preferred (002) orientation (Fig. S2). The observed lattice constants for **4** also lie in between that for hexagonal osmium (2.160 Å) and hexagonal ruthenium (2.142 Å), consistent with the replacement of osmium atoms in the hexagonal structure by the smaller ruthenium atoms. The increase in the lattice constant for **4**-500 compared with **4**-400 is also consistent with the EDX data, which suggested a more osmium-rich film for the former. The reason for the higher osmium content film obtained with a higher substrate temperature is not clear.

Conclusion

The compound $RuOs_3(CO)_{13}(\mu\text{-}H)_2$, **4**, has been demonstrated to be a suitable single-source precursor for the preparation of thin films of Os–Ru binary alloy. The ratio of osmium to ruthenium varied with the deposition temperature, and at higher temperatures the deposited surface was smoother. Osmium thin films have also been successfully obtained with **1, 2** and **3** as precursors, at 400 and 500 °C. The osmium thin films formed have a preferred (002) orientation.

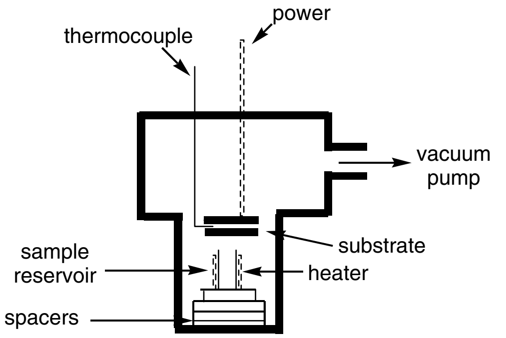

Figure 6. Schematic diagram of chemical vapour deposition apparatus.

Experimental

The clusters $Os_2(CO)_6(\mu\text{-}I)_2$ (**2**),[10] $Os_3(CO)_{12}Br_2$ (**3**)[11] and $RuOs_3(CO)_{13}(\mu\text{-}H)_2$ (**4**)[12] were prepared according to reported procedures. The compounds $Os_3(CO)_{12}$ (**5**) and $Ru_3(CO)_{12}$ (**6**) were purchased from Oxkem Ltd and used as supplied.

Surface morphologies of the samples were studied with a Philips XL30-FEG (field emission gun) scanning electron microscope (SEM), equipped with an ion getter pump (IGP). EDX studies were performed with an EDX analyzer attached to the SEM, at a working distance of 10 mm. Voltage and spot size were adjusted to make the counts per second (cps) in the range of 1000–2000. X-ray power diffraction (XRD) studies were performed using a Philips X'Pert diffractometer, PW3040 ($\lambda_{Cu,K\alpha} = 0.15418$ nm), on finely ground samples using a continuous 2θ scan mode from 35 to 90° in steps of 0.02°.

The CVD apparatus used is shown schematically in Fig. 6. Prior to evaporation, the silicon surfaces were cleaned in accordance to standard procedure.[13] The metal carbonyl compound (50 mg) was placed in the sample reservoir and loaded into the CVD chamber, together with a silicon wafer as the substrate, and then the system evacuated at 10^{-5} torr. Deposition temperature was set at 400 or 500 °C, and the deposition time was typically adjusted to about 15 min.

Supporting information

Supporting information may be found in the online version of this article.

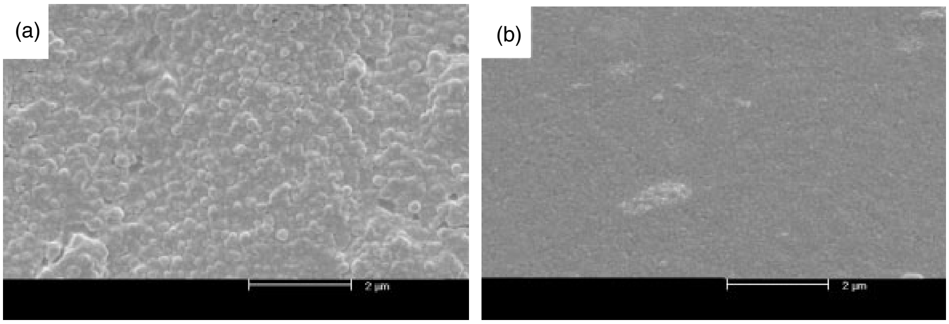

Figure 5. SEM images of (a) **4**-400 and (b) **4**-500.

Acknowledgments

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