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Low temperature chemical vapour deposition of ruthenium and ruthenium dioxide on polymer surfaces

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Thin films of ruthenium or ruthenium dioxide can be prepared on polymer films supported on aluminium disks by chemical vapour deposition (CVD) from the volatile precursor ruthenium tetroxide, RuO_4, by using hydrogen as reducing carrier gas. On very thin (*ca.* 0.7 μm) spin-cast polymer films on aluminium, ruthenium metal was deposited under mild conditions. These ruthenium films were crystalline when formed on polyurethane or poly(methyl methacrylate) but mostly amorphous when formed on polystyrene or poly(ether/ester)polyurethane block copolymers. On thicker polymer films (*ca.* 75 μm), the films formed were composed primarily of RuO_2 with lesser amounts of ruthenium metal. The films were characterized by using XPS, Auger, XANES, XRD and SEM techniques.

Introduction

This paper is concerned with the formation by chemical vapour deposition (CVD) of thin films of either ruthenium metal or ruthenium dioxide on polymer substrates, a topic which is of interest in materials research for several reasons. Both ruthenium and ruthenium dioxide have low resistivity and high thermal stability and so are useful in electronic applications.[1,2] For example, the electronic properties of ruthenium dioxide, in combination with its efficient diffusion barrier properties and ability to enhance polarisation fatigue of ferroelectric films when used as a contact electrode, make RuO_2 very attractive as a bottom electrode in thin film capacitors.[1–3]

Ruthenium dioxide films have previously been deposited on various substrates by reactive sputtering and related methods,[4] but also by CVD techniques,[1,5–7] while films of ruthenium metal have also been grown by CVD.[8,9] The first report of the CVD of films of RuO_2 utilised the precursor complexes $[Ru(acac)_3]$ (acac = MeCOCHCOMe), $[Ru(\eta\text{-}C_5H_5)_2]$ and $[Ru_3(CO)_{12}]$.[1] Typically, pyrolysis of $[Ru(acac)_3]$ at 600 °C with oxygen as carrier gas at 1 Torr produced RuO_2 having some carbon impurity, whereas deposition at 600 °C with hydrogen as carrier gas gave a film containing both Ru and RuO_2 phases. Likewise, $[Ru(\eta\text{-}C_5H_5)_2]$ gave films of RuO_2 and a mixture of ruthenium and ruthenium dioxide on silica and silicon substrates respectively, by CVD in the presence of oxygen at 575–600 °C. Resistivity values in the range 89.9–643 μΩ cm were observed for the films of RuO_2, and can be compared to the resistivity of 35–50 μΩ cm for bulk RuO_2.[1] Subsequent studies using the precursor $[Ru(C_5H_5)_2]$ showed that selective formation of RuO_2 could be achieved by using a low deposition rate in the presence of excess oxygen.[6] The β-diketonate derivative $[Ru(dpm)_3]$ (dpm = $Bu^tCOCHCOBu^t$) is more volatile than $[Ru(acac)_3]$ and has been used as a precursor for CVD of RuO_2 in the temperature range 275–425 °C.[5] At the lower end of this temperature range, the RuO_2 films could be formed in the (110) or (101) orientation, but at higher temperature the films were randomly oriented. The mildest conditions for CVD of RuO_2 are obtained by using the volatile precursor RuO_4 (mp 27 °C, bp 129 °C)[10] which has been shown to give high quality films at 150–220 °C on either glass or silicon substrates.[7] The decomposition is particularly simple [eqn. (1)] and so gives films of RuO_2 that are free of carbon impurity.

$$RuO_4 \rightarrow RuO_2 + O_2 \tag{1}$$

The CVD of films of metallic ruthenium ($\rho_{Ru} = 6.7$ μΩ cm) has been carried out by using the precursors $[Ru(acac)_3]$, $[Ru(\eta\text{-}C_5H_5)_2]$, $[Ru_3(CO)_{12}]$ or $[Ru(CO)_4(CF_3CCCF_3)]$ at temperatures in the range 175–500 °C, usually under reducing conditions with hydrogen as carrier gas,[1,8,9] and has potential applications in forming electrical contacts.[11] Both ruthenium and ruthenium dioxide make good diffusion barriers on either aluminium or silicon at temperatures as high as 600 °C.[11]

There is current interest in the metallization of polymer substrates by using CVD, but there are difficulties in terms of the temperature needed for CVD on thermally sensitive or low-melting polymer substrates and in terms of poor adhesion of 'inorganic' films on organic substrates.[12] The use of RuO_4 as a CVD precursor for metallization of polymers appeared to be promising for two reasons. First, it had already been shown that RuO_4 could act as a precursor for films of RuO_2 on inorganic substrates at moderate temperatures.[7] Second, the use of RuO_4 as a fixative and stain in TEM studies of both saturated and unsaturated polymers is well established,[13] and probably involves direct reaction with sites of unsaturation or with C–H bonds on the polymers with reduction of ruthenium.[13,14] This surface reaction should then give a chemical bond between the organic substrate and the forming film of ruthenium or ruthenium dioxide and so should lead to good adhesion to the polymer. This paper reports the results of a study of CVD of ruthenium or ruthenium dioxide on polymer substrates, in which the carrier gas hydrogen was used to facilitate the CVD reaction.

Experimental

Aqueous RuO_4 (**CAUTION**)[†] was obtained commercially (0.5% w/w solution, Strem Chemicals). Pure RuO_4 was prepared by extraction from aqueous RuO_4 using pentane at −30 °C, followed by evaporation of the pentane under vacuum

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[†] RuO_4 is volatile and toxic. It must be handled in a well-ventilated fume hood. Pure RuO_4 has been reported to explode when heated above 100 °C and it may react violently with organic substrates.

(10^{-3} Torr, −40 °C). Because of the very limited stability of pure RuO_4, it was prepared immediately before use. The evaporation of the pentane solution was carried out in the precursor reservoir itself to eliminate problems in subsequent transfer of the toxic, reactive substance.

Preparation of polymer substrates

The polymers used in this study (Chart 1) were obtained commercially (Aldrich). A solution of the polymer in tetrahydrofuran (THF, 0.2 µL, 3–5% w/w) was spin coated onto a thin disk of aluminium (0.5 mm thick × 1 cm in diameter) under vacuum at a speed of 2500 rpm to give a polymer film of thickness 0.7 ± 0.1 µm. Alternatively, a thicker sheet of the polymer (thickness 75 ± 10 µm) was formed by slowly adding a solution of the polymer in THF (0.5 mL) to the aluminium disk at room temperature and pressure and allowing the solvent to evaporate. Poly(methyl methacrylate) (PMM) and polystyrene (PS) had molecular weights $M_w = 996\,000$ and 280 000, respectively. Four different polyurethane based polymers were used as defined in Chart 1. The polyurethane (PU1), obtained from Thermedics, is a medical grade aromatic polymer with $M_w = 250\,000–300\,000$ g mol^{-1}. The polymers PU2, PU3 and PU4 (Chart 1) are block copolymers of the same polyurethane with polyether, polyester or mixed polyether/polyester units respectively and have similar molecular weights and melt index values of 16, 13 and 35, respectively.

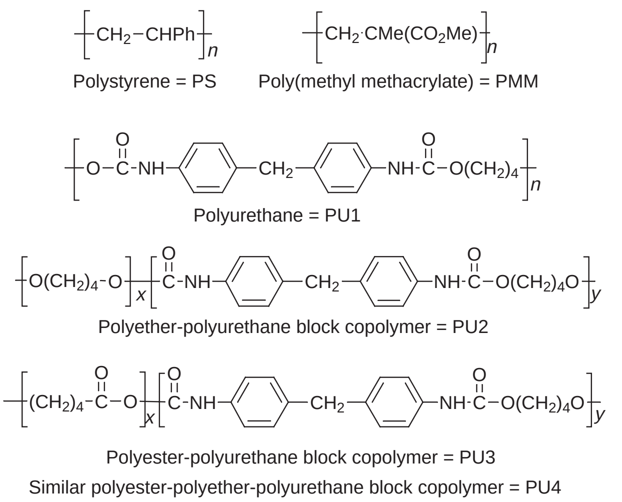


Chart 1 Structures of the polymers.

CVD procedure

Chemical vapour deposition experiments were carried out using a vertical cold-wall reactor at atmospheric pressure. The reactor consists of a quartz reaction chamber/reservoir with a carrier gas inlet and outlet near the bottom and top, respectively. The substrate was fixed to a central probe using high purity silver paint and was heated by using a thermostatted external rod heater. The precursor was kept at room temperature while the substrate was maintained at a fixed temperature in the range 23–100 °C during the CVD procedure. In a typical CVD experiment, films of thickness of *ca.* 1 µm could be grown in 30 min when using pure RuO_4 as precursor or 3 h when using aqueous RuO_4. The carrier gas was hydrogen in most experiments at a flow rate of 40–60 mL min^{-1}; the chamber was flushed with hydrogen before introduction of the precursor.

Analysis of the films

X-Ray photoelectron spectra (XPS) were obtained by using a SSL SSX-100 model XPS instrument with a monochromatized Al-Kα X-ray source (1486.6 eV). All the films were cleaned by argon sputtering at a beam energy of 4000 eV prior to collecting the data. Analytical data are given in Tables 1 and 2. The experimental binding energy (E_b) values are calibrated with respect to the C 1s binding energy at 284.6 eV. AES scans were recorded using a Perkin-Elmer PHI 600 Scanning Auger Multiprobe instrument with an electron beam energy of 3 keV. X-Ray absorption near-edge structure (XANES) at the Ru L-edge were recorded at the Canadian synchrotron radiation facility (CSRF) at the synchrotron radiation center, University of Wisconsin; a double crystal monochromator equipped with InSb(111) crystals was used to record the data. EDX/SEM micrographs were taken by using a Hitachi S4500 field emission SEM instrument. The X-ray diffraction patterns were obtained using a chromium X-ray source ($\lambda = 2.2896$ Å). Film thicknesses of ruthenium were determined by using a Sloan Dektak II profilometer, after creating a crater by Auger depth profiling. SEM cross-section micrographs were used to determine the thicknesses of RuO_2 films. The film resistivity was measured with a standard FPP5000 four-point probe instrument.

Results

Previously, it was shown that CVD from the precursor RuO_4 at 150–200 °C, either under vacuum or at atmospheric pressure with air as carrier gas, gave films of ruthenium dioxide on inorganic substrates including glass, silicon and aluminium.[7] In the present work, CVD studies were carried out by using the precursor RuO_4, with hydrogen as reducing carrier gas, on polymeric substrates using a simple vertical cold-wall reactor. The precursor RuO_4 is volatile and was readily transported in the gas phase at room temperature; it was used either as the aqueous solution obtained commercially or as the pure compound. The polymer films were supported on aluminium disks and were prepared in two ways. Either very thin films of

Table 1 CVD conditions and XPS analysis data for ruthenium films on polymers[a]

			Atom%		XPS/binding energy		
Precursor[b]	Substrate[a]	Substrate temperature/°C	Ru	O	Ru 3d$_{5/2}$	Ru 3d$_{3/2}$	O 1s
A	PS	25	98	2	280.6	284.4	530.7
A	PMM	65	100	0	279.8	283.9	abs
A	PU1	70	99	1	280.4	284.4	531.7
A	PU2	70	96	4	280.2	284.3	531.8
A	PU3	100	97	3	279.8	283.8	531.7
A	PU4	80	100	0	280.6	284.1	abs
B	PMM	60	99	1	280.4	284.2	531.8
B	PU2	70	96	4	280.3	284.5	532.7
B	PU3	100	97	3	280.6	283.9	532.6

[a]The substrate was a spin coated polymer (see Chart 1 for structures) of thickness *ca.* 0.7 µm supported on an aluminium disk. [b]Precursor: A, aqueous RuO_4 solution; B, pure RuO_4.

Table 2 CVD conditions and XPS analytical data for RuO_2 films[a]

			XPS binding energy		
Precursor[b]	Substrate[a]	Substrate temperature/°C	Ru $3d_{5/2}$	O 1s	Ru : O
A	PS	60	281.5	530.5	1 : 2.1
A	PU1	60	281.6	531.7	1 : 1.7
B	PS	25	280.9	531.5	1 : 1.6
B	PS	60	281.3	531.3	1 : 1.9
B	PU1	25	281.3	531.4	1 : 1.7
B	PU1	60	280.8	530.9	1 : 1.9

[a]The substrate was a film of polymer (see Chart 1 for structures) of thickness *ca.* 75 µm supported on aluminium. [b]Precursor: A, aqueous RuO_4 solution; B, pure RuO_4.

thickness 0.7 ± 0.1 µm were prepared by spin coating under vacuum or films of thickness 75 ± 10 µm were prepared by evaporation of the appropriate polymer solution in tetrahydrofuran on the aluminium disk. The CVD was then carried out at temperatures from room temperature to 100 °C and selected data are given in Tables 1 and 2.

A major difference was observed for CVD on the thin and thick polymer films respectively, while the different types of polymers gave similar results. Thus, the films formed on the thin, spin-coated polymer films were shiny and metallic in appearance, suggesting the formation of metallic ruthenium, while films on the thick polymer films were dark grey in colour, suggesting formation of ruthenium dioxide. These conclusions were supported by analytical data discussed below. In all cases, the films were strongly adherent to the polymer films and the Ru– or RuO_2–polymer films could be peeled off the aluminium support as a single unit. The combined films were much more rigid than the original polymer films.

XPS analysis

The XPS data for ruthenium films on spin-coated polymers are given in Table 1. The spectra contained single peaks for the Ru $3d_{5/2}$ and $3d_{3/2}$ binding energies, with the binding energy of Ru $3d_{5/2}$ = 279.4–280.4 eV and spin orbit splitting of 4.0 ± 0.2 eV, in agreement with literature values.[15] The chief problem is in calibrating the spectra, since the C 1s peak appears very close to the Ru $3d_{3/2}$ peak.[15] Ths peak could be observed before the films were sputtered but not afterwards, and the problem with calibration accounts for the range of observed binding energies. The peak overlap also made it difficult to establish the degree of carbon impurity in the ruthenium films from the XPS analysis. In most of the films, some oxygen impurity was present at a level of 0–5 atom%. The O 1s binding energies for metallic oxides and hydroxides are in the range 528–530 and 529.5–531.5 eV, respectively,[15] while the ruthenium films gave oxygen impurity peaks in the range 531.2–532.0 eV (Table 1). This suggests that the oxygen is present largely as hydroxide, though the calibration problem causes some uncertainty.

A typical XPS spectrum for a film of RuO_2 on a thick polymer film (PU1, Chart 1) is shown in Fig. 1(b). The Ru binding energies are similar in Ru and RuO_2 and there is again overlap of the Ru $3d_{3/2}$ and C 1s peaks, which makes calibration of the spectra difficult. The $3d_{5/2}$ binding energy for RuO_2 standard is in the range 280.5–281.5 eV, in good agreement with values of 280.8–281.6 eV reported in Table 2. There is fine structure in the Ru 3d peaks due to shake-up effects, as expected for ruthenium dioxide, but not for ruthenium metal films.[16] The atomic ratio Ru : O was 1.9 ± 0.2 in these films (based on the Ru $3d_{5/2}$: O 1s intensity ratio), consistent with the composition RuO_2. It is immediately

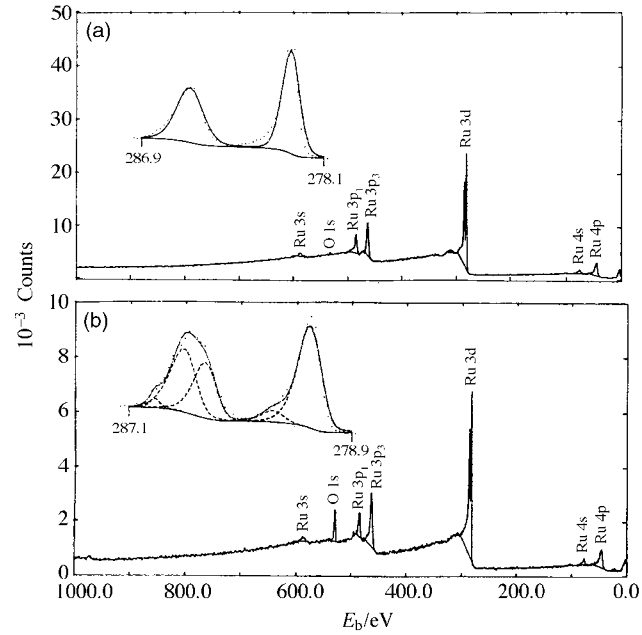


Fig. 1 XPS spectra of films: (a) ruthenium film grown on spin coated polystyrene at room temperature; (b) ruthenium dioxide film grown on polyurethane PU1 at 70 °C. In each case, the inset shows the fitted Ru 3d peaks.

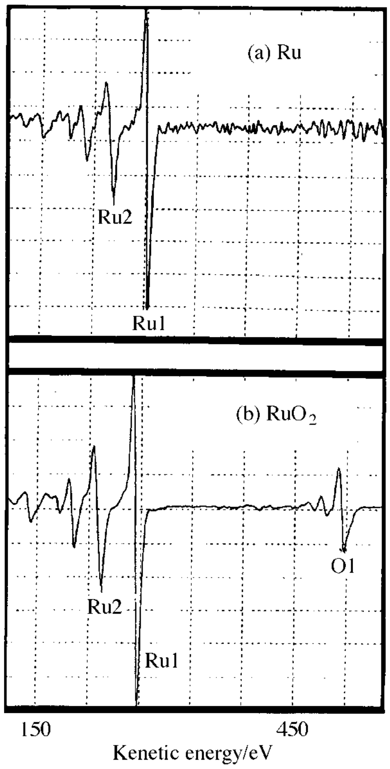


Fig. 2 Auger electron spectra of the films: (a) ruthenium film grown on polystyrene at room temperature; (b) ruthenium dioxide film grown on polyurethane PU1 at 70 °C. Both films were etched for 10 s before collecting the data.

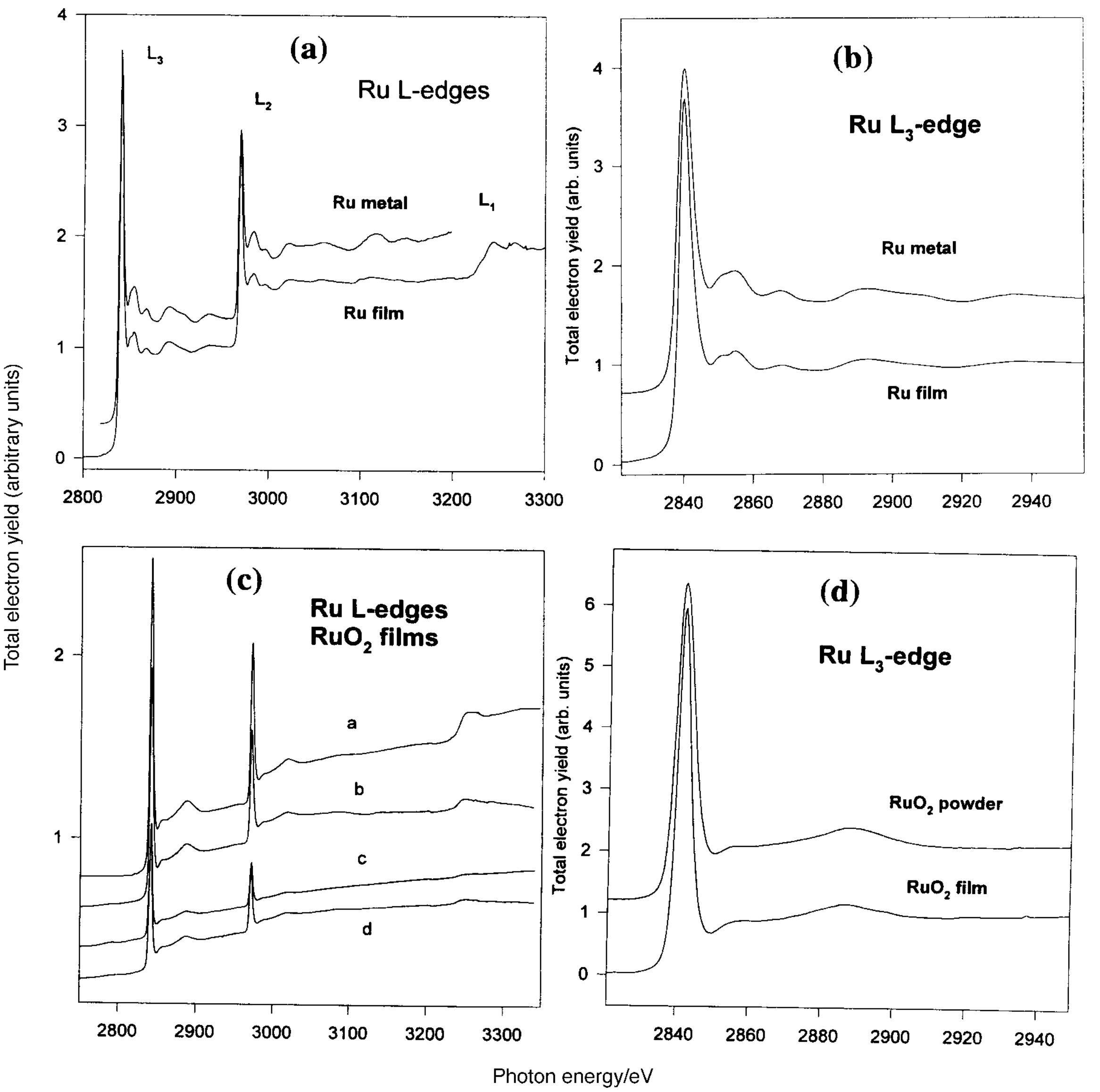


Fig. 3 XANES of Ru and RuO_2 films. (a) Comparison of Ru L-edge XANES for Ru metal standard and Ru film grown on spin cast polystyrene film at room temperature. (b) Ru L_3-edge XANES for the same samples (note that the spectral features for the thin film are slightly sharper than those of the metal standard, as is commonly observed for thin films *versus* bulk samples, an effect known as the 'thickness effect'). (c) Ru L-edge XANES for a series of films of RuO_2 of varying thickness. The films are defined by the polymer substrate/temperature of deposition as follows: (a) PU1 at room temperature; (b) polystyrene at room temperature; (c) polystyrene at 60 °C; (d) PU1 at 60 °C. Some spectra are shifted vertically for clarity. The edge jumps are as-measured and are normalized to photon flux. The thickness of the film can be gauged from the size of the edge jump (a > b > d > c). (d) Ru L_3-edge XANES normalized to unit edge jump for the RuO_2 standard and for the thin film of spectrum c in Fig. 3(c).

obvious by comparison of Fig. 1(a) and (b) that there is a major difference in the oxygen contents of the two samples.

AES analysis

Typical AES spectra obtained for Ru and RuO_2 films after etching for 10 s are shown in Fig. 2. The difference in intensity of the oxygen peaks in the two samples is immediately apparent. In the AES spectra, there is overlap of the carbon KLL line and the ruthenium MNN line at 273 eV,[1,17] but there is no overlap with the second Ru MNN line. Hence, by comparing the relative intensities of the Ru MNN peaks at 231 eV (Ru2) and at 273 eV (Ru1) with those of a pure ruthenium standard, it is possible to estimate the extent of carbon incorporation in the films. For pure ruthenium the ratio Ru1/Ru2 = 2.63,[17] whereas the ratio in either Ru or RuO_2 films was in the range 2.62–2.65. These data indicate that the films contain little carbon impurity. The Auger spectra were also used to study the compositional uniformity through the film thickness by depth profiling, and good uniformity was observed.

X-Ray absorption near edge spectra

Typical Ru L-edge XANES spectra, including spectra for ruthenium and ruthenium dioxide standards for comparison, are shown in Fig. 3. The spectra for both Ru and RuO_2 exhibit a spike (whiteline) at the $L_{3,2}$ edge (p to d transition) but not at the L_1 edge (s to p transition) [Fig. 3(a), (c)]. It is well established that the L_3 edge whiteline intensity is extremely sensitive to d band occupation, with higher intensity indicating a higher population of d-holes.[18–21] The absorption features in the near edge region for films developed on 0.7 µm spin-cast polymer substrates exhibit a sharp jump followed by two small resonances [Fig. 3(b)], and the close similarity with the corresponding features for the ruthenium metal standard immediately suggests that this film is comprised of ruthenium metal. Similarly, comparison of the XANES features for the films grown on 75 µm polystyrene films with those for a ruthenium dioxide standard [Fig. 3(c), (d)] supports the characterization as RuO_2 in this case.[22] The band assignments in this case are as follows. The L_3 white line is due to the transition $Ru(2p_{3/2})$–Ru-O(π*, mostly Ru d-character), the

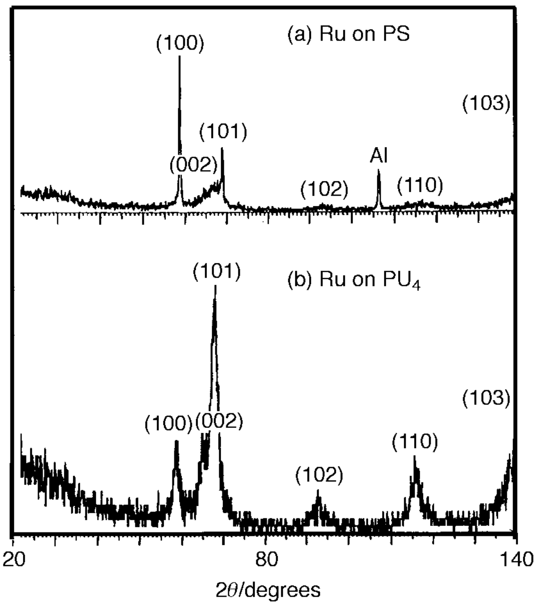
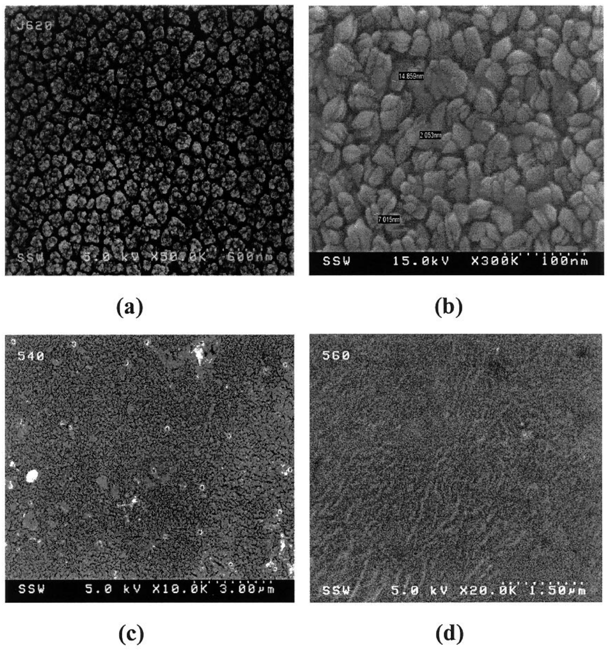


Fig. 4 X-Ray diffraction (Cr-Kα radiation) for ruthenium metal films grown on spin-cast polymer films: (a) film grown on polystyrene at room temperature; (b) film grown on PU4 at 65 °C.



(a) (b)

(c) (d)

Fig. 5 Scanning electron microscopic images of the films: (a) ruthenium metal film grown on spin-cast polyurethane PU1 at 70 °C from aq. RuO_4, showing the separated metal clusters; (b) similar ruthenium metal film grown on spin-cast polymer PU3 at 100 °C from aq. RuO_4, showing the individual metal crystallites on one cluster; (c) RuO_2 film grown on polystyrene at 60 °C from pure RuO_4; (d) RuO_2 film grown on polyurethane PU1 at 60 °C from pure RuO_4.

small shoulder at *ca.* 8 eV above the whiteline is due to the transition Ru($2p_{3/2}$)–Ru-O(σ*, mostly s–p character), and the broad oscillation at *ca.* 50 eV above the whiteline arises as a result of multiple scattering transitions (shape resonance). The intensities vary with the film thickness, each following the sequence $a > b > d > c$ in the spectra of Fig. 3(c).

Overall, the XANES results support the conclusions derived above from the XPS and AES data. The differences between the XANES of Ru and RuO_2 are not great enough to allow detection of minor impurities of one of these materials in the other, however.

XRD analysis

X-Ray diffraction patterns for the ruthenium metal films are shown in Fig. 4, and peak positions are in good agreement with literature values for polycrystalline ruthenium films.[23] For the ruthenium film on polystyrene, Fig. 4(a), the (100) orientation is predominant, but on other polymers [*e.g.* Fig. 4(b) for ruthenium on polymer PU4, Chart 1] the grains are randomly oriented.

The diffraction patterns for the RuO_2 films formed on thicker polymer films were broad and weak, but the expected (200), (210) and (111) reflections of RuO_2 were clearly resolved. In some samples, a very weak peak was also observed that was assigned to the hexagonal Ru metal (100) peak, indicating some minor impurity of metallic ruthenium in the films. It is clear that the RuO_2 films are largely amorphous and diffract only weakly. This is not surprising considering the low temperatures at which the films were formed.

SEM and conductivity studies

The thin film morphologies were studied by SEM and selected images are given in Fig. 5. Typical films of ruthenium metal on polyurethane are shown in Fig. 5(a) and (b). These consist of crystalline clusters, in which each cluster has dimensions of 100–150 nm in diameter and contains individual grains of dimensions 10–20 nm. The films on poly(methyl methacrylate) had a similar appearance with a grain size of 30–60 nm but films on polystyrene had a more regular, flatter appearance, though still with visible grain edges.

For a ruthenium film of thickness 0.2 µm on spin-cast polystyrene, the four-point probe resistivity measurement gave a value of 258 µΩ cm, whereas a ruthenium film of thickness 0.75 µm gave a resistivity of 1032 µΩ cm. The high values probably result from the non-uniformity of the films, with poor interconnections between the individual clusters as described above.

In contrast to the crystalline ruthenium films [Fig. 5(a) and (b)], the films of RuO_2 on polymers [Fig. 5(c) and (d)] showed no detectable crystalline character or structural features. Cross-sections of the ruthenium dioxide films, taken after peeling the film (polymer + RuO_2) from the aluminium disk, also showed no structural features and exhibited poor conductivity. These data are fully consistent with the XRD data, which also showed that the films are largely amorphous RuO_2.

Discussion

Ruthenium tetroxide is a very powerful oxidizing agent and reacts rapidly with many organic substances with oxidation of unsaturated groups or C–H bonds, forming ruthenium dioxide and organic oxygen functional groups at the surface of the organic material. These reactions have been used in the past for staining polymers for subsequent TEM studies,[13,14] but no applications in polymer metallization appear to be known. This work has shown that on thick polymer films supported on aluminium, and with hydrogen as carrier gas, films of RuO_2 can be grown which are strongly adherent to the polymer surface. It is proposed that a chemical bond (probably C–O–Ru) is formed between surface organic oxygen functional groups and the initial RuO_2 units formed at the polymer surface and that this anchors the growing RuO_2 film to the polymer. In this way, the common difficulty in forming adherent metal coatings arising from the low surface energy and reactivity of organic polymers is overcome. Another approach to coating organic polymers has been to activate the surface by use of ozonolysis or oxygen plasma to introduce surface oxygen functionality to which the inorganic film can bind.[18] In a sense, the RuO_4 precursor acts as its own surface activator by direct reaction with the polymer and so the pre-treatment step is not needed. Clearly, the ruthenium tetroxide could also be used as an alternative pre-treatment method for other forms of metallization. Under the conditions used in this work, the hydrogen carrier gas allows CVD on thick polymer films at lower temperature than is possible in air[7] but it does not cause significant reduction of ruthenium dioxide to metallic ruthenium. Bulk ruthenium dioxide is a dark blue–black compound but thin films are often dark grey in colour. Those formed in this work were dark grey and mostly amorphous as shown by XRD.

In contrast, the CVD precursor RuO_4 gave films of ruthenium metal under similar experimental conditions on very thin spin-coated polymer films supported on aluminium disks. The most likely explanation for this dramatic difference is that there is electrochemical coupling between the forming film and the supporting aluminium disk under these conditions, perhaps brought about by the ability of RuO_4 to penetrate the surface of the organic polymers, and this leads to oxidation of aluminium and reduction of RuO_2. The stoichiometry cannot be determined under these experimental conditions and so the role of hydrogen or aluminium in this reduction to ruthenium metal remains speculative.

In terms of applicability, good films were grown from either pure RuO_4 or from its aqueous solution. The chief advantage of the aqueous solution is that it is stable and commercially available, whereas pure RuO_4 is very reactive and toxic, and hence difficult to store and potentially hazardous to handle. Provided that the substrate is not water-sensitive, the use of aqueous RuO_4 is therefore recommended.

Acknowledgements

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